

**UNCLASSIFIED**

---

**AD 402 419**

*Reproduced  
by the*

**DEFENSE DOCUMENTATION CENTER**

**FOR**

**SCIENTIFIC AND TECHNICAL INFORMATION**

**CAMERON STATION, ALEXANDRIA, VIRGINIA**



---

**UNCLASSIFIED**

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

63-3-2

AMRL-TDR-63-7

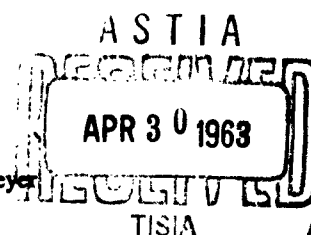
402 419

## CARBON DIOXIDE REDUCTION SYSTEM

TECHNICAL DOCUMENTARY REPORT NO. AMRL-TDR-63-7

January 1963

Life Support Systems Laboratory  
6570th Aerospace Medical Research Laboratories  
Aerospace Medical Division  
Air Force Systems Command  
Wright-Patterson Air Force Base, Ohio



Contract Monitors: R. E. Bennett and C. M. Meyer  
Project No. 6373, Task No. 637302

[Prepared under Contract No. AF 33(616)-8223

by  
G. A. Remus  
R. B. Neveril  
J. D. Zeff  
MRD Division  
General American Transportation Corporation  
Niles, Illinois]

UNCLASSIFIED BY ASTIA

AC AD NO.

402419

## **NOTICES**

**When US Government drawings, specifications, or other data are used for any purpose other than a definitely related government procurement operation, the government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise, as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.**

**Qualified requesters may obtain copies from ASTIA. Orders will be expedited if placed through the librarian or other person designated to request documents from ASTIA.**

**Do not return this copy. Retain or destroy.**

**Stock quantities available at Office of Technical Services, Department of Commerce, \$2.25.**

### **Change of Address**

**Organizations receiving reports via the 6570th Aerospace Medical Research Laboratories automatic mailing lists should submit the addressograph plate stamp on the report envelope or refer to the code number when corresponding about change of address.**

<p>Aerospace Medical Division 6570th Aerospace Medical Research Laboratories, Wright-Patterson AFB, Ohio Rpt. No. AMRL-TDR-63-7. CARBON DIOXIDE REDUCTION SYSTEM. Final Report, Jan 63, vi + 83 pp incl illus., tables, 4 refs. Unclassified report</p> <p>An automatically operated carbon dioxide re- duction system was designed, fabricated and tested. The system will reduce 0.365 pounds of carbon dioxide per hour, equivalent to a 3.2 man carbon dioxide output, and is required for providing respiratory support for man on ex- tended space missions. The program was con- ducted in three phases, analysis of a reactor developed on a previous</p> <p>( over )</p>	<p>Aerospace Medical Division 6570th Aerospace Medical Research Laboratories, Wright-Patterson AFB, Ohio Rpt. No. AMRL-TDR-63-7. CARBON DIOXIDE REDUCTION SYSTEM. Final Report, Jan 63, vi + 83 pp incl illus., tables, 4 refs. Unclassified report</p> <p>An automatically operated carbon dioxide re- duction system was designed, fabricated and tested. The system will reduce 0.365 pounds of carbon dioxide per hour, equivalent to a 3.2 man carbon dioxide output, and is required for providing respiratory support for man on ex- tended space missions. The program was con- ducted in three phases, analysis of a reactor developed on a previous</p> <p>( over )</p>	<p>UNCLASSIFIED</p> <ol style="list-style-type: none"> <li>Carbon Dioxide Reduction System</li> <li>Closed Cycle Ecological System</li> <li>Ecology</li> <li>Space Flight</li> </ol> <ol style="list-style-type: none"> <li>AFSC Project 6373 Task 637302</li> <li>Life Support Systems Laboratory</li> <li>Contract AF 33(616)-8223</li> <li>MRD Division, General American Transportation Corp.</li> </ol> <p>UNCLASSIFIED</p>
<p>contract, experimental determina- tion of design parameters, and fabrication and testing of an improved engi- neering model. Operating characteristics, feed gas compositions, recycle flow rates, reaction temperatures and pressures, and catalyst composition and configuration were established and the effects of variations in these were determined. Recommendations are made for improving the system and for future work.</p>	<p>contract, experimental determina- tion of design parameters, and fabrication and testing of an improved engi- neering model. Operating characteristics, feed gas compositions, recycle flow rates, reaction temperatures and pressures, and catalyst composition and configuration were established and the effects of variations in these were determined. Recommendations are made for improving the system and for future work.</p>	<p>UNCLASSIFIED</p> <ol style="list-style-type: none"> <li>G. A. Remus, R. B. Neveril, J. D. Zeff</li> <li>In ASTIA collection</li> <li>Aval fr OTS:\$2.25</li> <li>Secondary report no. GATC Report No. MR-1163-50</li> </ol> <p>UNCLASSIFIED</p>

## **FOREWORD**

**This project was initiated by the Life Support Systems Laboratory of the 6570th Aerospace Medical Research Laboratories, Aerospace Medical Division, Wright-Patterson Air Force Base, Ohio. The project was begun by the Mechanics Research Division as a subsidiary of the American Machine and Foundry Company and was completed by the MRD Division as a subsidiary of the General American Transportation Corporation. The research was conducted under Contract AF 33 (616)-8223, Project No. 6373, "Equipment for Life Support in Aerospace," and Task No. 637302, "Respiratory Support Equipment." This work was monitored by Messrs. R. E. Bennett and C. M. Meyer of the Life Support Systems Laboratory. This study began in April 1961 and was completed in August 1962.**

**This report is cataloged by the General American Transportation Corporation as Report MR 1163-50.**

## ABSTRACT

An automatically operated carbon dioxide reduction system was designed, fabricated and tested. The system will reduce 0.365 pounds of carbon dioxide per hour, equivalent to a 3.2-man carbon dioxide output, and is required for providing respiratory support for man on extended space missions. The program was conducted in three phases, analysis of a reactor developed on a previous contract, experimental determination of design parameters, and fabrication and testing of an improved engineering model. Operating characteristics, feed gas compositions, recycle flow rates, reaction temperatures and pressures, and catalyst composition and configuration were established and the effects of variations in these were determined. Recommendations are made for improving the system and for future work.

## PUBLICATION REVIEW

This technical documentary report has been reviewed and is approved.

*Wayne H. McCandless*  
WAYNE H. McCANDLESS  
Chief, Life Support Systems  
Laboratory

# TABLE OF CONTENTS

<u>SECTION</u>		<u>Page No.</u>
1	INTRODUCTION .....	1
	1.1 Program Objectives .....	1
2	ANALYTICAL PROGRAM .....	2
	2.1 Chemical Equilibrium Theory .....	2
	2.2 Mathematical Model .....	3
	2.3 Graphical Equilibrium Data .....	5
	2.4 Summary .....	12
3	EXPERIMENTAL PROGRAM .....	14
	3.1 Testing .....	14
	3.2 Battelle System .....	14
	3.3 Experimental System .....	16
	3.4 Experimental Tests .....	18
	3.5 Summary of Test Results .....	23
4	ENGINEERING MODEL .....	31
	4.1 Design Requirements .....	31
	4.2 Overall System and Flow Diagrams .....	31
	4.3 Reactor and Carbon Collector .....	36
	4.4 Heat Exchanger-Water Condenser .....	39
	4.5 Water Separator .....	40
	4.6 Recycle Pump .....	41
	4.7 Controls and Instrumentation .....	42
	4.8 System Assembly and Preparation for Operation .....	46
	4.9 System Operation .....	49
	4.10 Engineering Model Test Results .....	51
	4.11 Weight, Power and Volume .....	57
	4.12 Summary on the Engineering Model .....	57
5	CONCLUSIONS AND RECOMMENDATIONS .....	60
	5.1 Conclusions .....	60
	5.2 Recommendations .....	61
6	REFERENCES .....	63



# TABLE OF CONTENTS (Cont.)

<u>SECTION</u>	<u>Page No.</u>
APPENDIX .....	64
Item 1 - Development of Equilibrium Constant, K, from Free Energy and Enthalpy Data .....	64
Item 2 - Compilation of Computer Data and Graphical Representation of Equilibrium Concentration .....	66
Item 3 - Insulation Optimization .....	68
Item 4 - Heat Exchanger Optimization .....	70

# LIST OF FIGURES

<u>Figure</u>	<u>Description</u>	<u>Page No.</u>
1	EQUILIBRIUM VOLUME FRACTION VS. O/H RATIO, 440°F .....	6
2	EQUILIBRIUM VOLUME FRACTION VS. O/H RATIO, 620°F .....	7
3	EQUILIBRIUM VOLUME FRACTION VS. O/H RATIO, 980°F. ....	8
4	EQUILIBRIUM VOLUME FRACTION VS. O/H RATIO, 1340°F .....	9
5	CO <sub>2</sub> -H <sub>2</sub> REACTION MODEL .....	10
6	CO <sub>2</sub> % CONVERSION VS. O/H RATIO, 9 PSIG .....	11
7	CO <sub>2</sub> % CONVERSION VS. REACTION PRESSURE, O/H RATIO 0.5 ...	13
8	ORIGINAL BATTELLE CO <sub>2</sub> REDUCTION SYSTEM FLOW DIAGRAM .....	15
9	MODIFIED CO <sub>2</sub> REDUCTION SYSTEM FLOW DIAGRAM .....	17
10	PHOTOGRAPH OF MODIFIED CO <sub>2</sub> REDUCTION SYSTEM .....	19
11	EXPERIMENTAL TEST NO. 12, GRAPHICAL RESULTS .....	21
12	CO <sub>2</sub> REDUCTION SYSTEM ASSEMBLY, PRELIMINARY DESIGN .....	32
13	REACTOR ASSEMBLY, PRELIMINARY DESIGN .....	33
14	CO <sub>2</sub> REDUCTION SYSTEM ASSEMBLY, FINAL DESIGN .....	34
15	CO <sub>2</sub> REDUCTION PROCESS BLOCK FLOW DIAGRAM .....	35
16	CO <sub>2</sub> REDUCTION PROCESS PICTORIAL FLOW DIAGRAM .....	38
17	PHOTOGRAPH OF REDUCTION SYSTEM ENGINEERING MODEL .....	59
18	SQUARE-TUBE HEAT EXCHANGER CROSS-SECTION .....	71
19	TEMPERATURE VS. LENGTH OF HEAT EXCHANGER FOR COUNTER-CURRENT FLOW .....	71

## SECTION 1

### INTRODUCTION

#### 1.1 Program Objectives

This report summarizes the engineering evaluation, final design, and fabrication and testing of an engineering model of an improved system to convert carbon dioxide to oxygen by hydrogen reduction for advanced aerospace vehicles. The overall scope of this research has been to evaluate an experimental carbon dioxide reduction system as developed by Battelle Memorial Institute in order to determine its capabilities, deficiencies, and operating characteristics and to design and fabricate an improved system that will have the following operating characteristics:

(1) The system must convert a minimum of 0.33 pounds of carbon dioxide (equivalent to the metabolic output of three men) per hour to water.

(2) The system must operate satisfactorily at 0 to 1-g condition and withstand 15-g force without damage. The system must withstand a vibration of 0.2 cps to 500 cps.

(3) The methods of feeding the reactants into the system must be such that methane buildup is held to a minimum without sacrificing the rate of carbon dioxide decomposition.

(4) Instrumentation of the improved system is to be adequate to indicate the satisfactory operation of the system. A fail-safe control shall be included to prevent the hazardous build-up of flammable impurities such as  $\text{CH}_4$  and  $\text{H}_2$ , and a means of removing undesirable contaminants shall also be included.

(5) The design of the improved system is to incorporate ease of maintenance, cleaning, and replacement of catalyst.

(6) The time for reaching system equilibrium must be minimum so that life can be sustained shortly after launch.

(7) The designed system must also be of minimum volume and have high reliability, a minimum power demand, and be of minimum weight. A long life expectancy is also required.

The engineering evaluation also specified the inclusion of an investigation of the influence of the type, shape, and quantity of the catalyst on the reaction; also the effect of catalyst agitation and internal heaters.

## SECTION 2

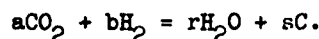
### ANALYTICAL PROGRAM

#### 2.1 Chemical Equilibrium Theory

When chemical compounds react with each other to give other chemical products the reaction will proceed until each of the initial reactants has decreased to a certain concentration and each of the products formed has increased from zero to a certain concentration. This phenomenon will occur for all chemical reactions if a sufficient length of time is allowed; however, the length of time required varies greatly from one reaction to another.

The concentrations existing at this point are referred to as equilibrium concentrations, and for gases reacting to form other gases may be measured as percentages by volume. These volume percentages are mathematically related to each other in a definite manner which is dependent upon the chemical equation written for the reaction, and upon a constant,  $K$ , which is determined from thermodynamic properties of the initial components and final products.

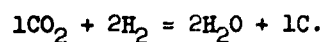
As an example, one chemical equation which can be written for the reaction between  $\text{CO}_2$  and  $\text{H}_2$ , is as follows:



The equilibrium equation relating the gas volume percentages, represented by the terms " $x$ ", and with  $\pi$  representing reaction total pressure, is:

$$\frac{(x_{\text{H}_2\text{O}})^r}{(x_{\text{CO}_2})^a (x_{\text{H}_2})^b} (\pi)^{r-a-b} = K$$

The concentration term for carbon,  $\text{C}$ , is not included since the carbon formed is a solid. To balance the chemical equation properly the coefficients,  $a$ ,  $b$ ,  $r$  and  $s$  are as follows:



The equilibrium equation then is:

$$\frac{(x_{\text{H}_2\text{O}})^2}{(x)^1 \text{CO}_2 (x_{\text{H}_2})^2} (\pi)^{2-1-2} = K$$

or

$$(x_{\text{H}_2\text{O}})^2 / (x_{\text{CO}_2}) (x_{\text{H}_2})^2 (\pi) = K$$

In actual chemical reaction if the values of  $K$  and of  $\pi$  are known, then the ratio of  $x_{H_2O}$  to  $x_{CO_2}$  and  $x_{H_2}$  may be determined. The constant,  $K$ , may be calculated from thermodynamic properties  $H_2$ ,  $CO_2$ ,  $H_2O$  and  $C$ , which are directly influenced by the reaction temperature. (The derivation of  $K$  for various reactions and temperatures is shown in Appendix A, Item 1.)

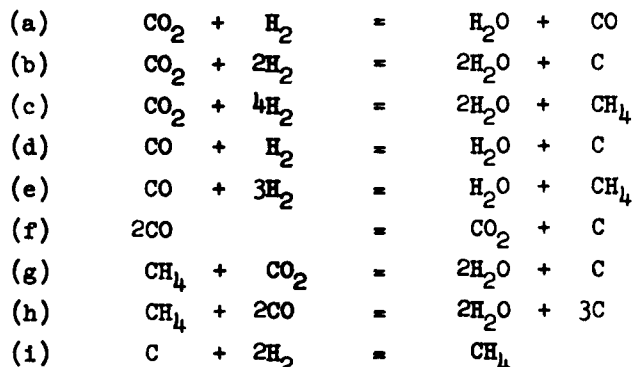
Because  $K$  is directly affected by the reaction temperature the equilibrium concentrations will be affected similarly by temperature.

The equilibrium concentrations of any of the gases in the above reaction will also be affected by the initial concentrations of  $CO_2$ ,  $H_2$  or  $H_2O$  gases. For instance, if there are equal amounts of  $CO_2$  and  $H_2$  initially, the  $CO_2$  equilibrium concentration,  $x_{CO_2}$ , will have a certain value, while if there were three times as much  $CO_2$  as  $H_2$  initially, the  $CO_2$  equilibrium concentration would have a higher value. This example merely approximates the relation between initial and equilibrium concentrations; the actual relation is of great importance and must be known exactly for reactions where the formation of an excess of one of the products is desired.

The analytical phase of the design study was therefore concerned with a mathematical analysis of the effects of temperature, pressure, and initial concentrations upon the final equilibrium concentrations of gaseous products from the reaction of  $CO_2$  and  $H_2$ . The primary objective of this analysis was to determine the conditions which permit maximum  $CO_2$  conversion.

## 2.2 Mathematical Model

In a system where  $CO_2$  and  $H_2$  react various products may be formed, and these products in turn may inter-react to give additional products. Many reactions are consequently possible in this system. Some of these are as follows:



Various other reactions could be written, including those where  $O_2$  might result from a reaction of  $CO_2$  or of  $H_2O$ , or where  $C_2H_6$  or higher hydrocarbons might result from polymerization of  $CH_4$ . However, at the temperature levels considered (1100°F to 1400°F) these other reactions can proceed only to a negligible extent. Therefore, in the system under study, the only six products assumed to be present will be  $CO_2$ ,  $H_2$ ,  $CO$ ,  $CH_4$ ,  $H_2O$  and  $C$ .

Examination of the above equations shows that several equations are actually the algebraic sums or differences of other equations. For example, equation (b) is the sum of (a) plus (d); equation (c) is the sum of (b) plus (i); equation (a) is (d) minus (f), etc. Any of the above equations may be

derived from a combination of other equations as long as all of the reactants and products are included in the basic starting equations. The two simplest reactions shown are (f) and (i); these include all reactants and products except  $H_2O$ . Equation (b) represents the overall reaction desired in the system under study, and includes  $H_2O$ .

Consequently reactions (b), (f) and (i) considered in simultaneous operation and equilibrium were assumed to completely represent all of the reactions which can occur in a  $CO_2$ ,  $H_2$ ,  $CO$ ,  $CH_4$ ,  $H_2O$  and  $C$  system up to  $1400^\circ F$ .

Based on these reactions, three equilibrium equations may be written in terms of an equilibrium constant,  $K$ , (which is a function of temperature), reaction pressure,  $\pi$ , and equilibrium concentrations,  $x$ , as gaseous volume fractions. These are:

1.  $K_1 = (x_{H_2O})^2 / (x_{CO_2})(x_{H_2})^2 \pi$  from equation (b).
2.  $K_2 = (x_{CO})^2 \pi / (x_{CO_2})$ , from reaction (f).
3.  $K_3 = (x_{CH_4}) / (x_{H_2})^2 \pi$ , from reaction (i).

These equations represent the relation between the volume fractions of the five gaseous components present at simultaneous equilibria for these reactions.

When certain volumes of  $CO_2$ ,  $CO$ ,  $H_2O$ ,  $CH_4$  and  $H_2$  gases react, there are fixed amounts of oxygen, hydrogen and carbon atoms in each gas. After the reaction has occurred these fixed amounts are still present, although not necessarily as part of the original component. Some oxygen originally part of  $CO_2$  may exist as part of  $CO$  or of  $H_2O$ ; similarly some hydrogen originally as pure  $H_2$  may exist as part of  $CH_4$ , or of  $H_2O$ . Letting initial gas concentrations be represented by  $a_n$ , and initial and final gas volume by  $V_I$  and  $V_F$  an atom balance may be written for both oxygen and hydrogen. (Carbon is not as easily represented, since some carbon converts from a gaseous product to pure solid carbon; however, the mathematical model for the reacting system does not require developing the carbon balance.)

$$\text{Oxygen: } V_I (2a_{CO_2} + a_{CO} + a_{H_2O}) = V_F (2x_{CO_2} + x_{CO} + x_{H_2O})$$

$$\text{Hydrogen: } V_I (2a_{H_2} + 2a_{H_2O} + 4a_{CH_4}) = V_F (2x_{H_2} + 2x_{H_2O} + 4x_{CH_4})$$

The coefficients for the volume fractions "a", and "x", correspond to the subscript in the chemical symbol for each gas, since the symbol represents actual atomic quantities of elements in the chemical component.

The ratio of oxygen to hydrogen atoms in the initial components is the same as in the equilibrium mixture, as follows:

$$(4) \quad \frac{O}{H} = \frac{V_I (2a_{CO_2} + a_{CO} + a_{H_2O})}{V_I (2a_{H_2} + 2a_{H_2O} + 4a_{CH_4})} = \frac{V_F (2x_{CO_2} + x_{CO} + x_{H_2O})}{V_F (2x_{H_2} + 2x_{H_2O} + 4x_{CH_4})}$$

This equation relates exactly the volume concentrations at equilibrium with initial concentrations. The "O/H" ratio thus developed is used to conveniently

describe the ratio of oxygen to hydrogen and holds true at all times, with the restriction that no material is added or removed during the reaction.

At any point during the reaction the total volume fractions of the gases present will equal unity:

$$(5) \quad a_{\text{CO}_2} + a_{\text{CO}} + a_{\text{H}_2\text{O}} + a_{\text{H}_2} + a_{\text{CH}_4} = 1.0$$

$$x_{\text{CO}_2} + x_{\text{CO}} + x_{\text{H}_2\text{O}} + x_{\text{H}_2} + x_{\text{CH}_4} = 1.0$$

In the development of the mathematical model up to this point, six unknowns have been introduced, the five equilibrium volume concentrations for  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{O}$ , and  $\text{CH}_4$ , and the O/H ratio. Only five equations numbered (1) through (5) above have been developed for handling these unknowns.

The primary objective of the mathematical analysis was to determine those conditions of temperature, pressure, and concentrations which would maximize the conversion of carbon dioxide. Consequently, an analysis, combining the five equations, was derived which would indicate the  $\text{CO}_2$  conversion at each selected temperature and pressure, but over a complete range of initial concentration conveniently expressed by the O/H ratio. In essence this process amounted to selecting a temperature and pressure to establish  $K_1$ ,  $K_2$ ,  $K_3$  and in equations (1), (2) and (3) and then designating a value for  $\text{O/H}$ , the initial concentration as measured by the oxygen to hydrogen ratio. A series of values for each of the equilibrium gas-volume concentrations could then be calculated.

At this point it was necessary to utilize the IBM 1620 computer at MRD to handle the solution of the equations, and to provide the necessary calculated concentration values. These solutions were then converted to a graphical representation. A typical set of equations and data for developing one graph at a given temperature and pressure are shown in Appendix A, Item 2.

### 2.3 Graphical Equilibrium Data

Four equilibrium graphs were compiled in this manner for temperatures ranging from  $440^\circ\text{F}$  to  $1340^\circ\text{F}$ , at 9.0 psig, with the O/H ratio varied from zero to infinity. These graphs are shown as Figures 1, 2, 3 and 4. From these graphs it can be seen that the line representing the equilibrium volume fraction of  $\text{H}_2\text{O}$  passes through a maximum value when the O/H ratio equals 0.50.

If the assumptions are made, that no water is initially present, that only the  $\text{CO}_2$ ,  $\text{H}_2$ , and  $\text{H}_2\text{O}$  gaseous concentrations change during the reaction, and that the reaction has proceeded until equilibrium prevails, then the volume fraction of  $\text{H}_2\text{O}$  formed when equilibrium is reached is a proportional measure of the amount of  $\text{CO}_2$  which has been converted in the reaction. Therefore the maximum  $\text{CO}_2$  conversion should occur under those conditions of temperature, pressure, and concentrations which give the maximum equilibrium  $\text{H}_2\text{O}$  concentration.

The overall reactor may be looked upon as a batch-type system where a given volume-mixture of gases enter, portions of some gases react while others do not but are merely present during the reaction, and a consequently different mixture leaves the reactor. The following block diagram illustrates this type of operation. (Figure 5 shows that the equilibrium volume concentrations at

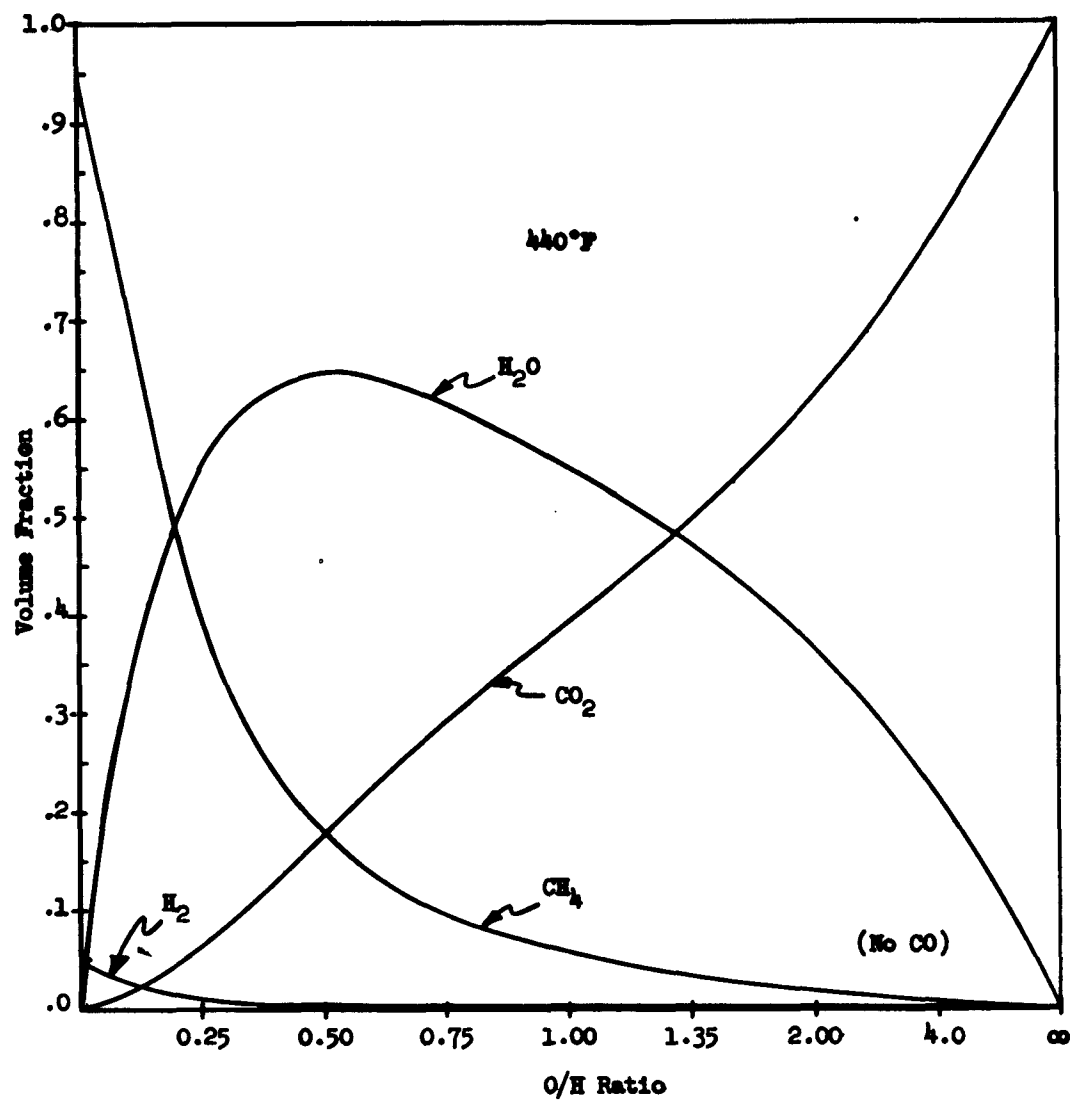


Figure 1  
EQUILIBRIUM VOLUME FRACTION VS. O/H RATIO, 440°F



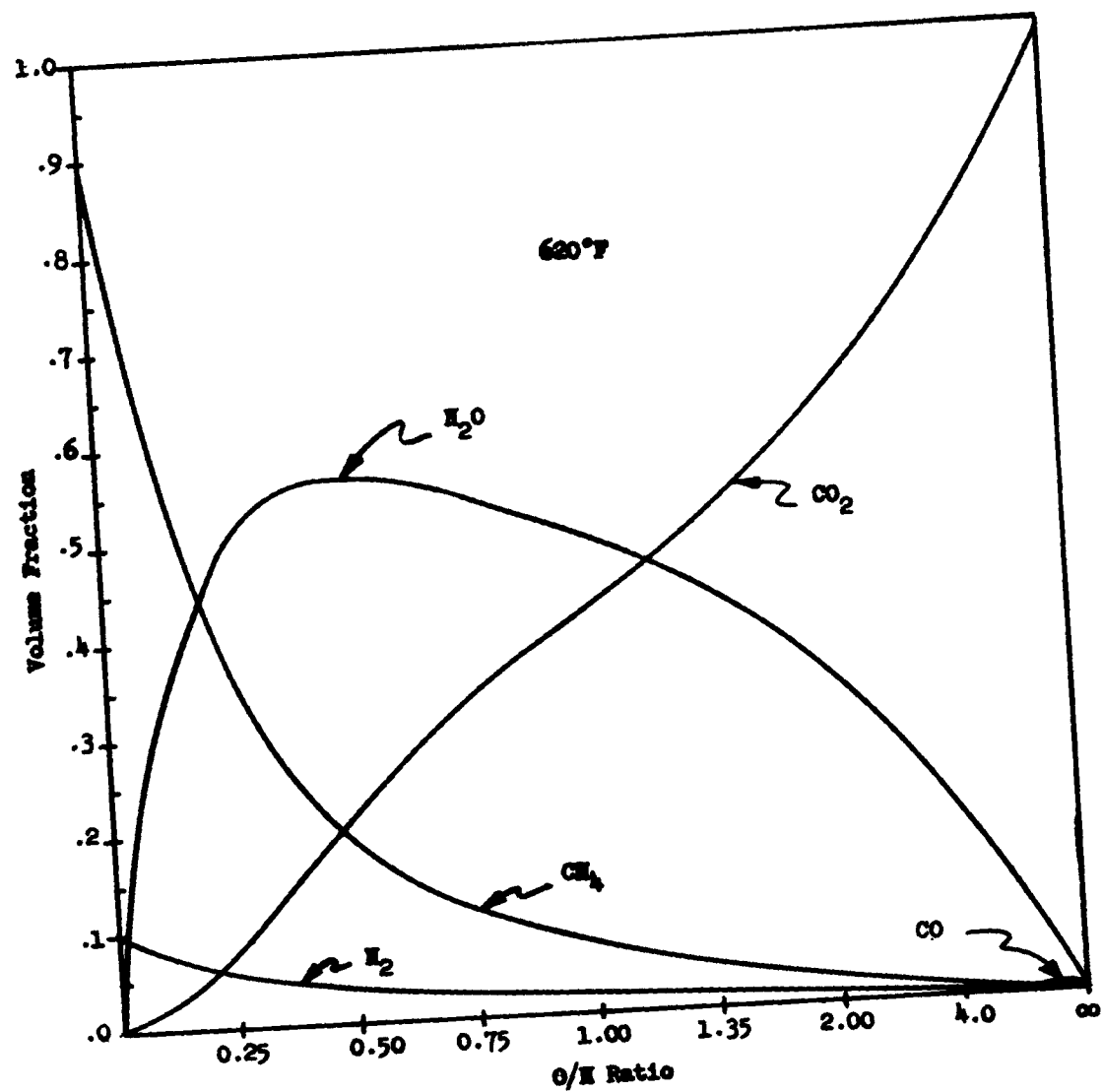


Figure 2  
EQUILIBRIUM VOLUME FRACTION VS. O/H RATIO, 620°F

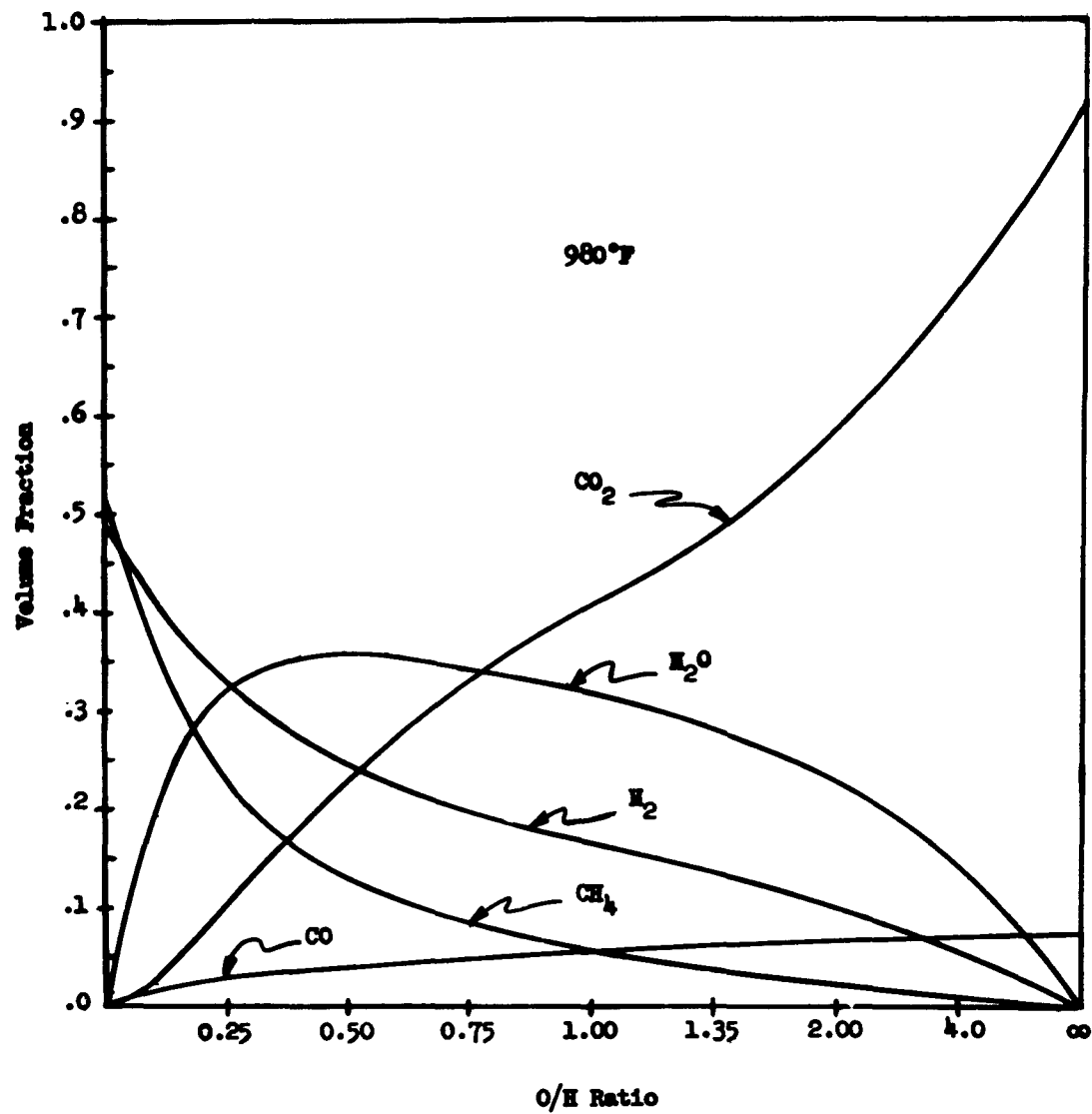


Figure 3  
EQUILIBRIUM VOLUME FRACTION VS. O/H RATIO, 980°F

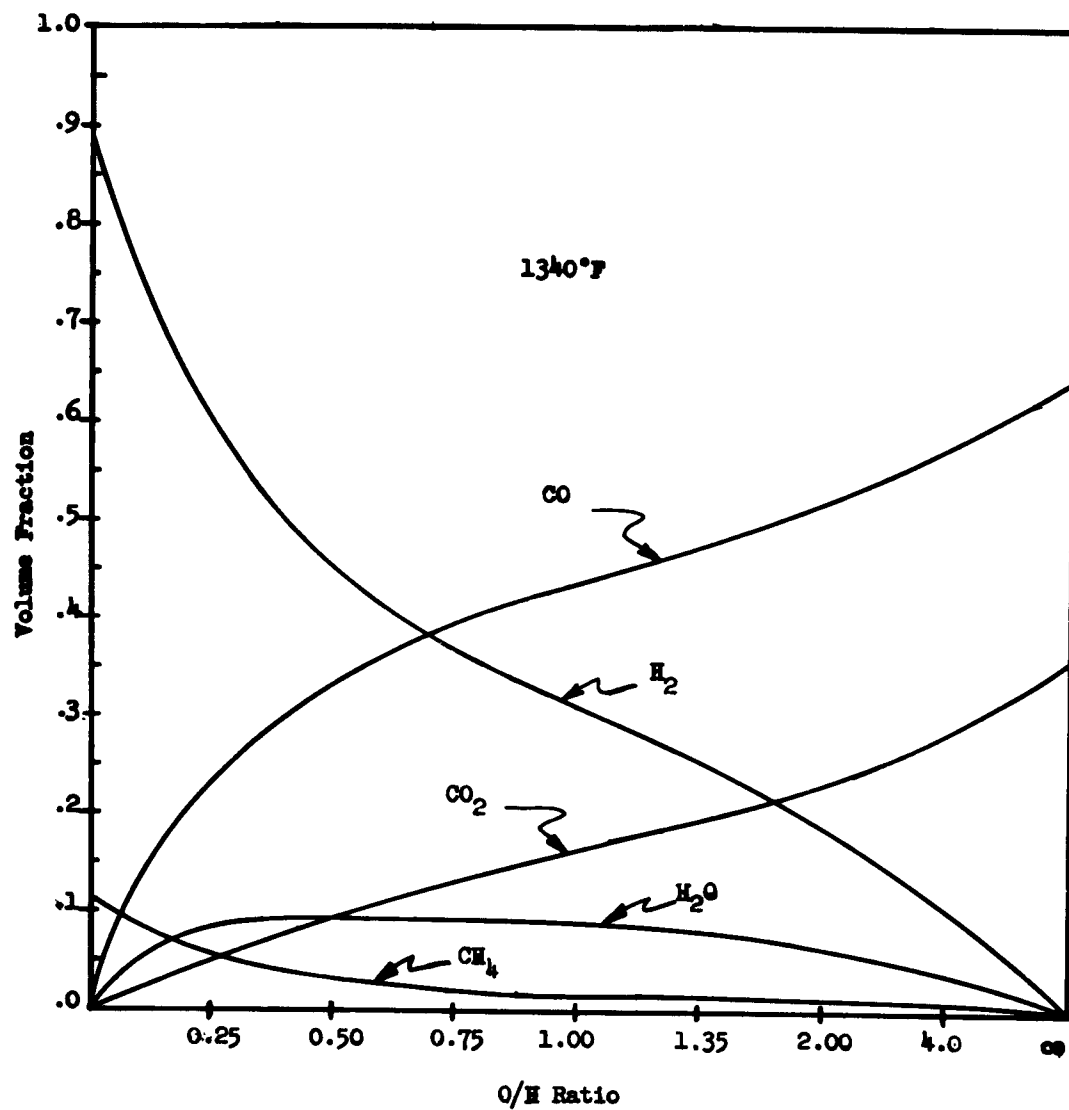


Figure 4  
EQUILIBRIUM VOLUME FRACTION VS. O/H RATIO, 1340°F

an O/H ratio of 0.50 are  $H_2 = 0.245$ ,  $CH_4 = 0.127$ ,  $CO_2 = 0.230$ ,  $CO = 0.040$ ,  $H_2O = 0.358$ . If there were no water entering the reactor then 0.358/2 volume units of  $CO_2$  and 0.358 volume units of  $H_2$  would have had to react to form the 0.358 units of  $H_2O$ .)

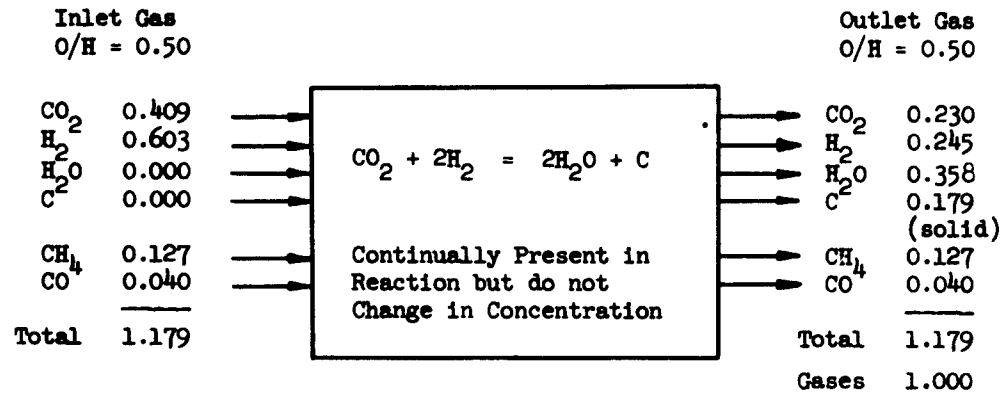


Figure 5 REACTION MODEL

The volume fraction of  $H_2O$  formed was 0.358. Therefore the volume of  $CO_2$  which reacted was 0.358/2 or 0.179 volume units. Because the equilibrium measurements correspond to gases leaving the reactor, the volume rate through the reactor is based on outlet conditions. Therefore the amount of  $CO_2$  converted is 0.179/1.000 or 17.9% of the total gas volume flow leaving the reactor.

Based upon this analysis, Figure 6 was plotted showing per cent of  $CO_2$  converted versus O/H ratio at varied temperatures between 440°F and 1340°F, but at a fixed pressure of 9.0 psig. The amount of  $CO_2$  converted is seen to be greater at lower reaction temperatures.

The gas composition entering the reactor in Figure 5 was assumed to contain no water. If some water were to enter the reactor with the inlet gases, then the amount of  $CO_2$  converted would decrease proportionately.

The equilibrium  $H_2O$  volume (based on a total of 1.000 volume units leaving the reactor) is 0.358 volume units. This  $H_2O$  resulted from the conversion of 0.179 volume units of  $CO_2$ . If the entering gas contained, for example, 0.020 units of  $H_2O$  then only 0.338 additional units could be formed in reaching equilibrium. This approximates 2.0%  $H_2O$  in the inlet stream. The amount of  $CO_2$  converted would decrease 0.010 units to 0.169. The per cent  $H_2O$  vapor by volume and the decrease in volume units of  $CO_2$  converted of saturated gases at 9.0 psig is shown in the following table:

Carbon Dioxide Conversion vs. % Water in Inlet Gas		
Reactor Inlet Gas Temp.	Inlet Gas, % $H_2O$ by Vol.	Decrease in Volume Units of $CO_2$ Converted
40°F	0.5	.0035
57°F	1.0	.0050
70°F	1.5	.0075
79°F	2.0	.0100
97°F	3.0	.0150
108°F	5.0	.0250

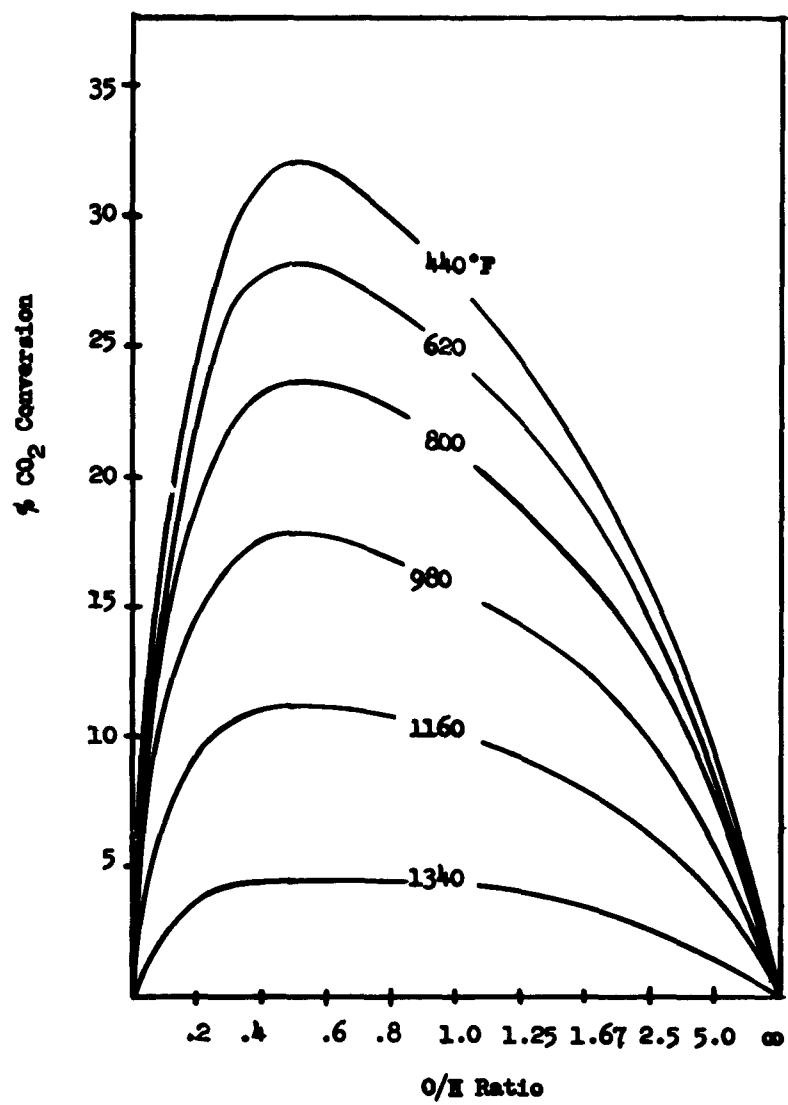


Figure 6  
CO<sub>2</sub> % CONVERSION VS. O/H RATIO, 9 PSIG

If 0.179 volume units is the maximum possible  $\text{CO}_2$  conversion, then conversion with an inlet saturated gas temperature at  $108^\circ\text{F}$  would result in a conversion of  $0.179 - 0.025 = 0.154$  units;  $0.154/0.179 = 0.86$ , or an efficiency of only 86%. These figures show the loss in efficiency due to high inlet gas temperatures; they also show the effects of cooler inlet temperatures.

The amount of  $\text{CO}_2$  converted (or the amount of  $\text{H}_2\text{O}$  at equilibrium) was found to be a maximum at an O/H ratio of 0.50. Consequently, this ratio was fixed in subsequent calculations, and the pressure was varied at different temperatures. These computations were also run on the IBM 1620 computer. On Figure 7 the per cent of  $\text{CO}_2$  converted is plotted versus pressure at various temperatures. This chart shows that the per cent of  $\text{CO}_2$  converted at a constant temperature and at an O/H ratio of 0.50, increases with increasing pressure, and that this effect becomes more pronounced as the reaction temperature increases.

#### 2.4 Summary

The analytical section of the Design Study of a  $\text{CO}_2$  conversion system consisted of a mathematical analysis of the effects of temperature, pressure and composition on the equilibrium concentrations resulting from the reaction of  $\text{CO}_2$  and  $\text{H}_2$ . The results of the analysis showed the amount of  $\text{CO}_2$  converted is (1) maximized when the O/H ratio = 0.50, (2) greater at lower reaction temperatures, (3) greater if inlet gases to the reactor contain lower amounts of water (this implies that lower condenser temperature is desirable in a recycle-system) and (4) greater at higher pressure, and that the effect of increased pressure is more pronounced at higher temperatures.

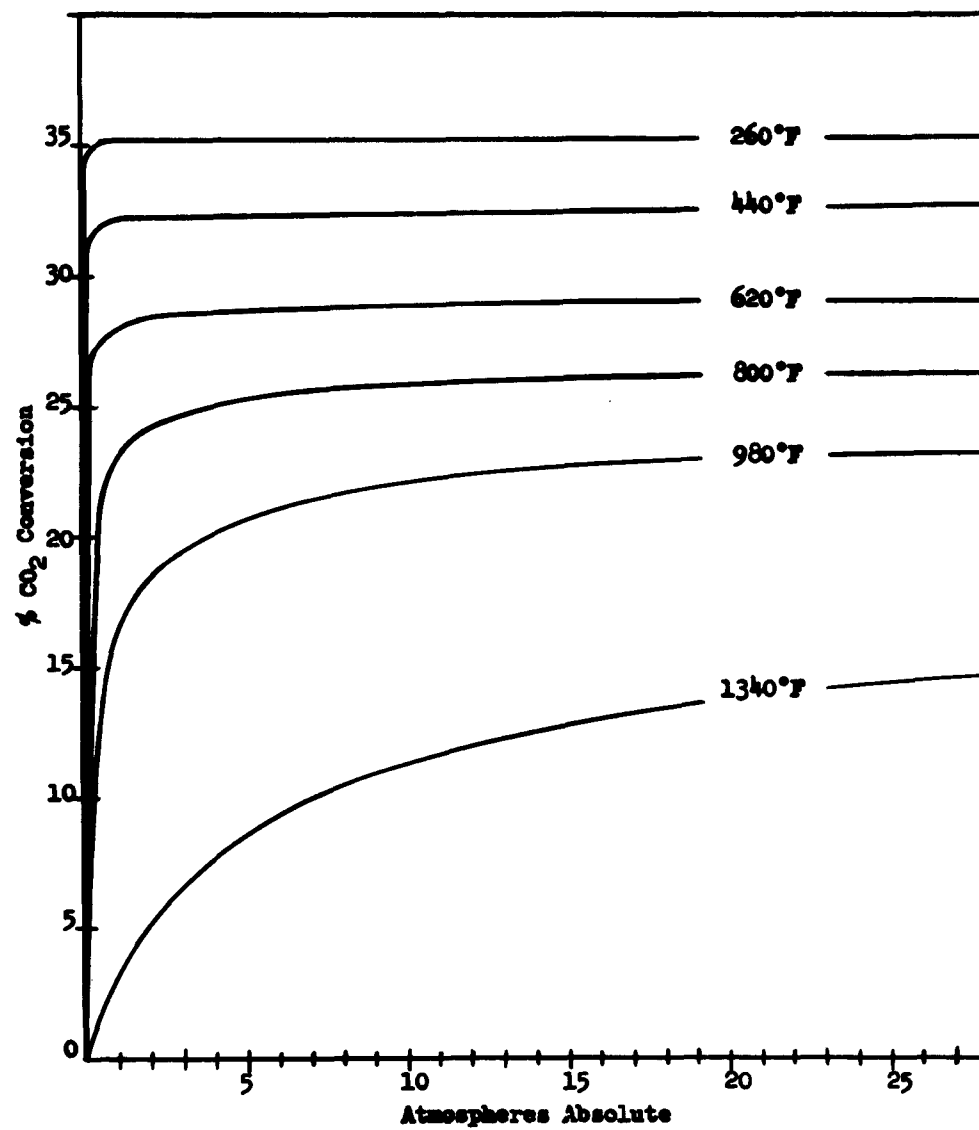


Figure 7  
CO<sub>2</sub> % CONVERSION VS. REACTION PRESSURE, O/H RATIO 0.5

## SECTION 3

### EXPERIMENTAL PROGRAM

#### 3.1 Testing

The experimental program was directed towards developing and improving existing  $\text{CO}_2$  conversion systems through actual testing and operation. The theoretical equilibrium data developed in the analytical section were used as criteria for setting process variables such as temperature and composition during various phases of testing. These data were particularly helpful in evaluating and controlling the actual effect on  $\text{CO}_2$  conversion as expressed by the O/H ratio.

As testing progressed process variables were continually and experimentally altered on the basis of their individual effects upon conversion rate, rather than on the basis of theoretical predictions. This is necessary because, although definite and reliable mathematical calculations can be made of equilibrium considerations, theoretical reaction rates cannot be predicted according to the present development of rate theory without an error factor of 10 to 100 or more.

#### 3.2 Battelle System

The preliminary phase of the experimental section covered familiarization with the  $\text{CO}_2$  conversion system originally built and operated by the Battelle Memorial Institute.

The Battelle system was arranged as shown in Figure 8. The major components of this system were the (1) feed sub-system, (2) reactor, (3) water condenser, (4) driers, (5) re-cycle gas pumps, (6) re-cycle throttle valve, and (7) re-cycle rotameter. The Feed Sub-System consisted of (1)  $\text{CO}_2$ - $\text{H}_2$  gas storage cylinder and high-pressure regulator, (2) low-pressure gas regulator, (3) feed rotameter, (4) feed wet-test gas-volume meter, (5) feed throttle valve and (6) feed pump.

The reactor was divided into three sections, the upper gas space, the middle catalyst section, and the lower heat-exchanger section. Incoming gases entered at the bottom of the reactor and rose through a bundle of tubes up the center of the reactor. Gas flow direction reversed in the upper 6" gas-space, and passed downwards through a 24"-long annular catalyst section, with a 3"-outer and a 1"-inner diameter. The catalyst section consisted of an upper 18" portion of steel-wool, and a lower 6" portion of commercial Girdler catalyst pellets, 1/4"-long by 1/4"-diameter. The complete catalyst section was heated by four separately controlled 6"-high nichrome wire heating coils wrapped on the outside of the reactor. The gases leaving the catalyst section continue down through a 12"-long heat-exchanger section approximately 1 inch in diameter; this section cools the gases leaving the catalyst and transfers the heat to incoming gases entering at the bottom of the reactor.

The water condenser consisted of an aluminum coil and a glass collecting bottle, both immersed completely in an ice-bath. The condenser removed water formed in the  $\text{CO}_2$  reduction from the gas stream leaving the reactor. The driers were fabricated from 2-inch aluminum pipe and contain calcium sulfate granules for further removal of water from the gases leaving the condenser. In the first Battelle design a condenser was not used, and all water formed was removed in the calcium sulfate driers. The system had two driers in parallel,



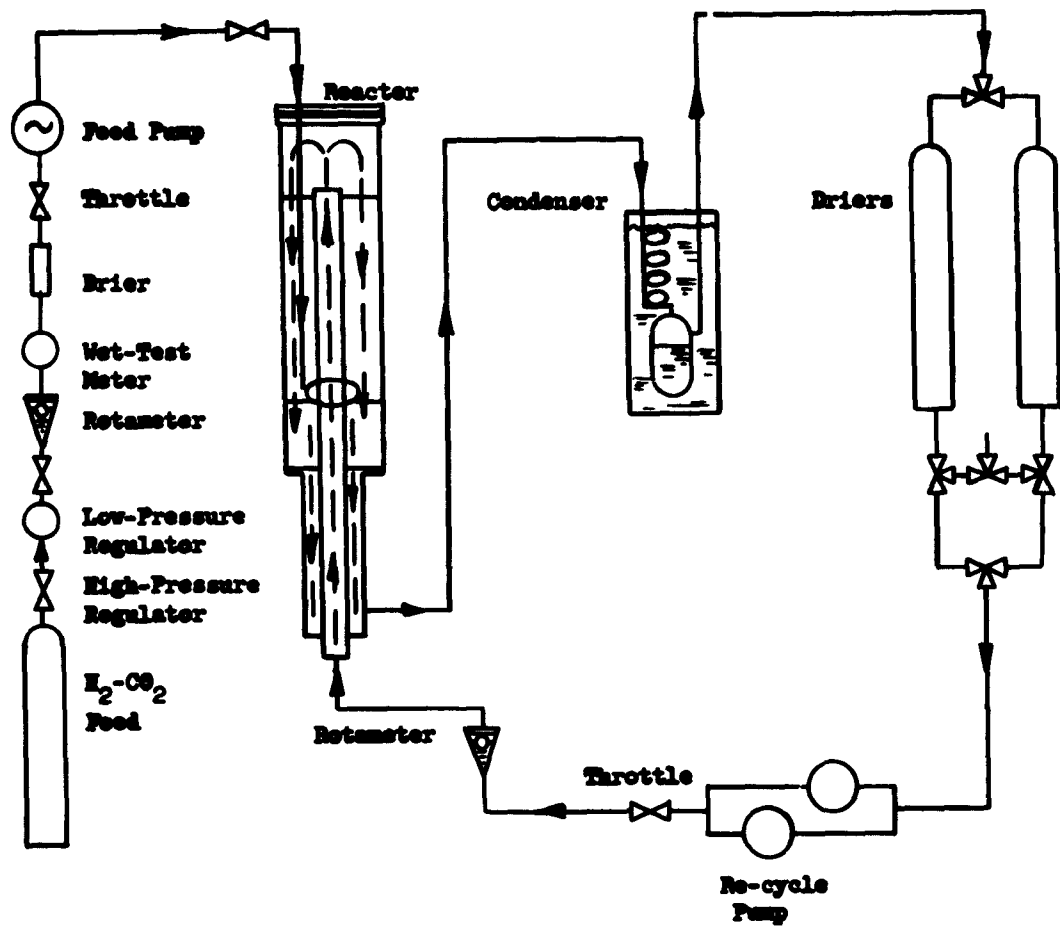


Figure 8  
ORIGINAL BATTELLE  $CO_2$  REDUCTION SYSTEM FLOW DIAGRAM

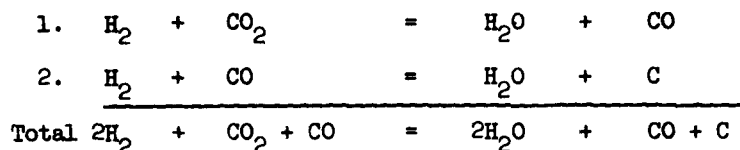
one in operation, the other idle or being desorbed by heating under vacuum. The condenser was added to increase the absorption cycle time of the driers.

Two diaphragm-type pumps in parallel were used to circulate the recycle gases through the system. A throttle valve on the outlet side of the pumps was used to regulate the recycle flow rate. A ball-type rotameter was used to measure this rate.

In the feed sub-system, the feed mixture of  $\text{CO}_2$  and  $\text{H}_2$  gas was stored in a high-pressure cylinder. Feed gas leaving the cylinder was reduced to lower pressures (5-10 psig) by a high-pressure regulator. The feed rate had to be measured with high accuracy since this rate would be a direct indication of the  $\text{CO}_2$  conversion rate. A wet-test gas-meter was used for this purpose. A drying column of calcium sulfate was placed in the outlet line from the meter to remove water absorbed from the meter. Because this type of meter must operate at a pressure between 0 inches and 6 inches of  $\text{H}_2\text{O}$  gauge, the feed gas pressure had to be lowered to this range, by a low-pressure gas regulator. A rotameter was used in the feed line as a rapid indicator of approximate flow rate for rough flow adjustments. A feed throttle-valve was placed in the exit line of the wet-test gas-meter for manually adjusting feed flow-rate to meet the demand created in the reactor during operation. Since the pressure in the reactor was maintained at 9.0 psig a feed-pump was required to raise the feed pressure from between 0 inches to 6 inches of  $\text{H}_2\text{O}$  to reactor pressure.

Feed entered the system through a tube at the top of the reactor which passed down into the catalyst; the height of the tube could be adjusted to allow injection of the feed at any point within the catalyst. The tube terminated in a perforated ring passing through the annular catalyst section, providing equal flow distribution of the feed.

In the last experiments at the Battelle Institute the feed-tube outlet-ring was at the interface between the steel-wool catalyst and the commercial Girdler catalyst pellets. This arrangement provided for the possibility that the  $\text{CO}_2$  conversion took place in two steps, although no definite indication of a two-step mechanism was actually shown. The upper steel-wool catalyst section was heated to an outside surface temperature of 525-550°C, and the lower Girdler pellet catalyst section to 700-750°C. The possible two-step conversion might be:



At the Battelle Memorial Institute the reactor was operated at 9 psig with the recycle pumps in parallel and the recycle throttle valve completely open. Battelle did not report the exact flow rate but subsequent metering of the system at MRD indicated that the flow through the reactor was approximately 0.65 SCFM or 18.4 liters/min. Under these conditions a  $\text{CO}_2$  conversion rate of 500 cc/min was achieved (0.13 lb/hr) or slightly over one-man capacity.

### 3.3 Experimental System

The Battelle reactor was tested at the MRD laboratories but with some modifications of several parts of the overall system. The modified system is shown in Figure 9.

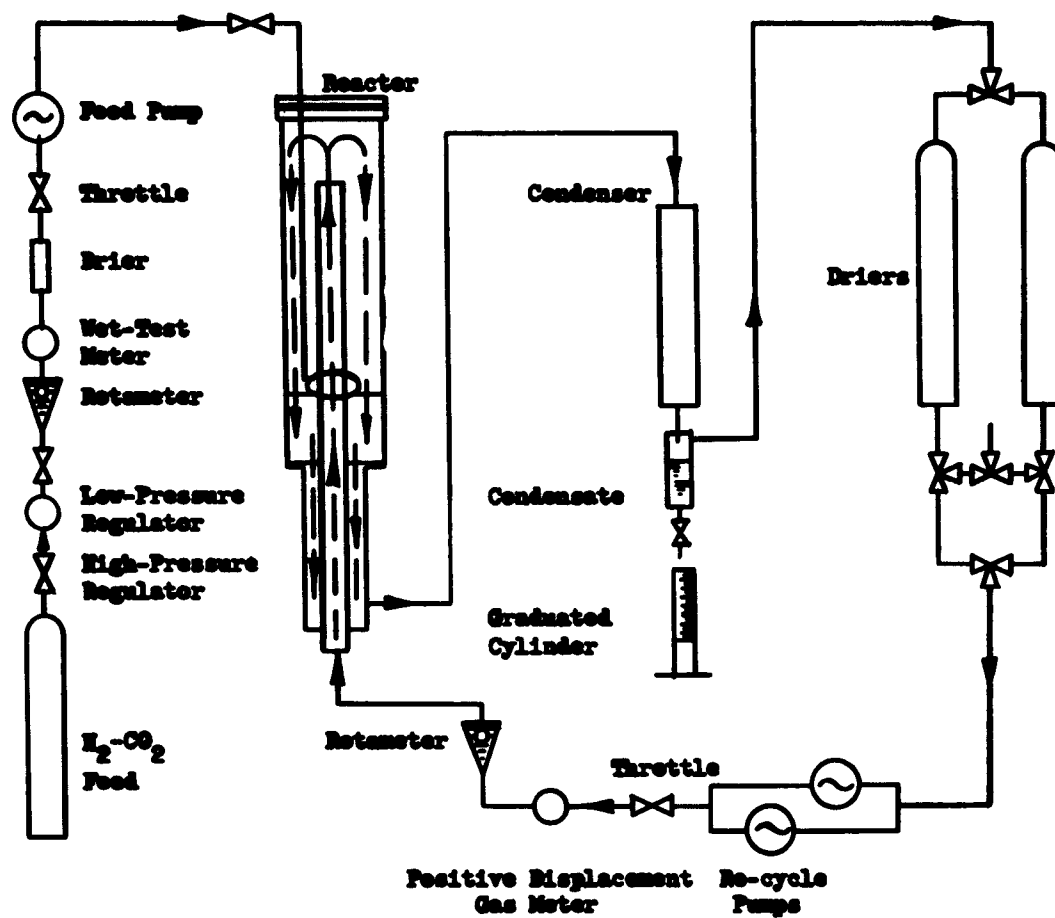


Figure 9  
MODIFIED CO<sub>2</sub> REDUCTION SYSTEM FLOW DIAGRAM

This system differs from the original Battelle system in that the condensate trap for water condensed from reacted gases was provided with a hand-valve for the periodic removal of the formed water. The water thus removed could be collected and measured and the actual rate of water formation could be calculated. This rate is a more accurate measurement of the  $\text{CO}_2$  conversion rate than the  $\text{CO}_2$  feed rate for the following reasons.

If the system has an undetected leak, then a false high reading will be noted in the  $\text{CO}_2$  gas feed rate, since, volume-wise, all of the gas leaking out will be replaced by feed gas. Also, until recycle gases reach equilibrium, some of the  $\text{CO}_2$  fed into the system will be retained in raising the  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{H}_2\text{O}$  concentrations to the proper levels. Neither a leak, nor the buildup to equilibrium conditions is reflected in the amount of  $\text{H}_2\text{O}$  formed, and consequently this measurement will provide a more representative indicator of  $\text{CO}_2$  conversion rates.

The system also differs in that a positive-displacement volumetric gas-meter was placed in the recycle gas line. This type of meter gives highly reproducible readings with an accuracy of 1 to 2% of the flow being measured; a rotameter at the low flow rates under consideration will give an accuracy of 1 or 2% of its full scale capacity and will give reproducible results only if viscosity, density, pressure, and temperature of flowing gases remain constant. The positive-displacement gas-meter reproducibly measures true volumetric flow regardless of density or viscosity, as long as temperature and pressure remain constant. (The viscosity and density of recycled gases change continually as composition changes.) Accurate measurement of the recycle rate was essential to gauging its effect on  $\text{CO}_2$  conversion rate, and could not have been made without a positive-displacement meter. A photograph of the modified system is shown in Figure 10.

### 3.4 Experimental Tests

#### Test Results - Nos. 1 to 3

The first three test runs on the reactor system were merely shakedown operations to test all components for operability, and to locate and eliminate leaks in the system. Also, calibrations were made with the gas chromatograph analyzing system.

#### Test Results - Nos. 4 to 9

The next group of six tests was concerned with a complete duplication of the final test run at the Battelle Institute. Several runs within this group also investigated (1) the possibility of running without the calcium sulfate driers, (2) the effects of starting the reactor with pure  $\text{CH}_4$  initially versus using a mixture of  $\text{CH}_4$  and  $\text{H}_2$ , and (3) properly preparing the steel-wool and Girdler pellet catalyst for the reaction by reducing with  $\text{H}_2$  at high temperatures.

In this group of tests the Battelle conversion rate of 500 cc/min was completely duplicated at a recycle rate of 0.65 SCFM, 9.0 psig, with the steel-wool section of the catalyst at 500° to 525°C, and the pellet catalyst section at 725° to 750°C. The gaseous composition as measured by O/H ratio was approximately 0.40. These runs also indicated qualitatively that the system could be operated without driers, but no measurements of loss in efficiency were made.

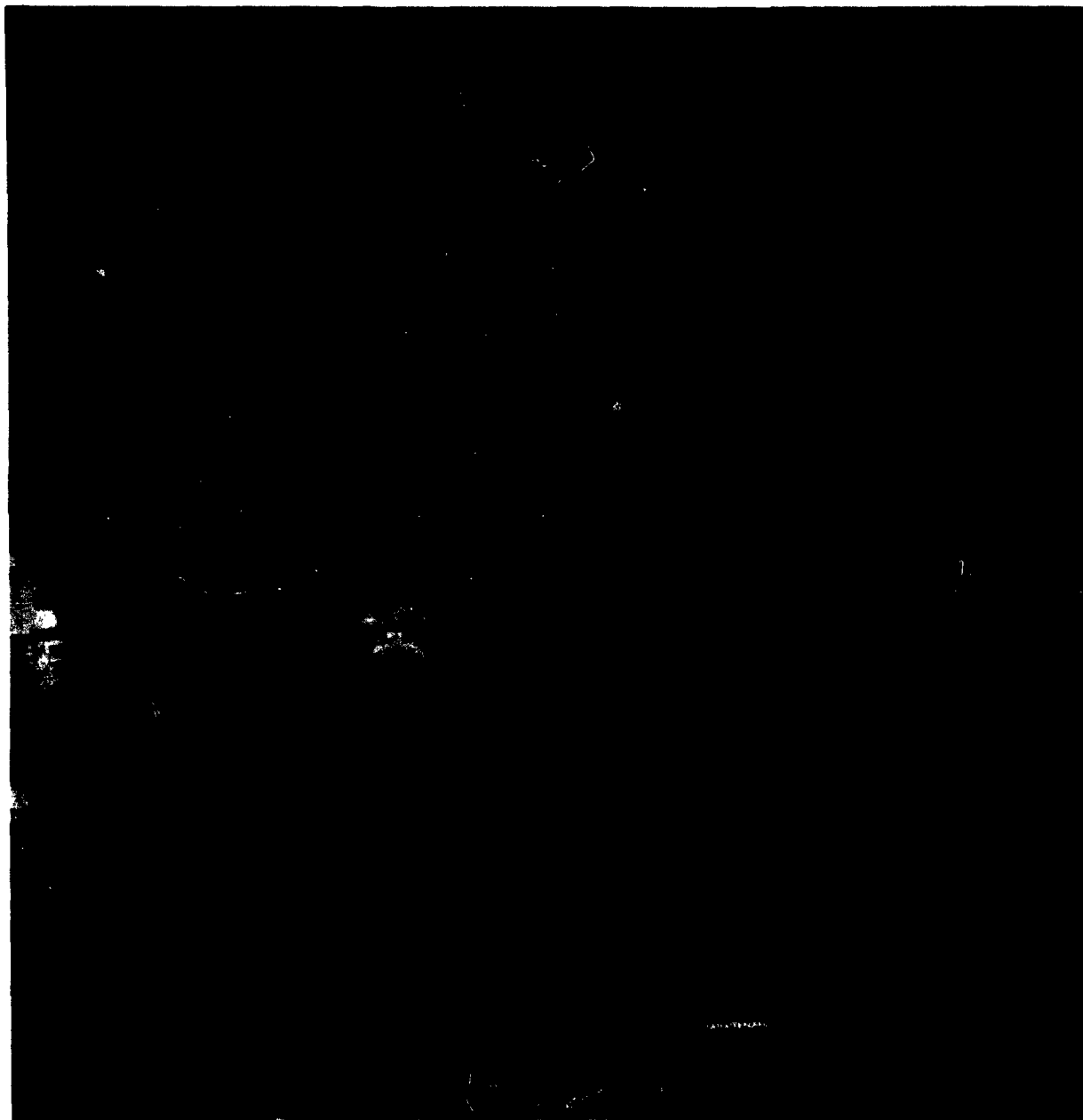


Figure 10  
PHOTOGRAPH OF MODIFIED CO<sub>2</sub> REDUCTION SYSTEM

In these runs, after some carbon was formed and remained in the reactor, the initial charge of  $\text{CH}_4$  (based on initial Battelle procedures) would decompose to form  $\text{H}_2$  and more C, with attendant pressure rise. It was determined that charging with a mixture of 80%  $\text{H}_2$  and 20%  $\text{CH}_4$  eliminated this pressure rise, and was used in subsequent runs. The first several tests in this group produced excessive build-up of  $\text{CO}_2$  and CO. This was due to inadequate reduction of the catalyst with  $\text{H}_2$ ; the  $\text{H}_2$  in the feed was reducing the catalyst instead of reacting with  $\text{CO}_2$ , so consequently  $\text{CO}_2$ , and equilibrium amounts of CO, were left in excess in the reactor. From this it appeared that the catalyst required at least twenty-four hours of reducing with pure  $\text{H}_2$  at temperatures between 600° and 700°C (1100° to 1300°F).

#### Test Results - Nos. 10 to 12

The next group of three tests sought to determine (1) whether the  $\text{CO}_2$  conversion was greater at lower temperatures, as indicated in the results of the mathematical analysis and, (2) the quantitative effect of operating without driers. In these tests the result of operating at lower temperatures showed that the  $\text{CO}_2$  conversion rate was approximately cut in half for each 140°C temperature decrease. This indicated that the reaction is predominantly influenced by kinetic or reaction mechanism considerations rather than by equilibrium considerations.

The results of operation without driers showed quantitatively that the  $\text{CO}_2$  conversion rate was 80% of the rate with driers. Driers in the process require a vacuum system, and a timed heating and valving system for switching one drier from onstream to offstream regeneration. The advantages of eliminating such systems far outweighed the gain in  $\text{CO}_2$  conversion. Consequently, driers were eliminated from all subsequent runs, and the condenser alone was used for water removal.

These runs also indicated that the maximum  $\text{CO}_2$  conversion rate was achieved when the O/H ratio rose to approximately 0.3, was maintained up to 0.5, and then fell off above 0.5. The maximum rate was restored when the O/H ratio was returned to between 0.3 and 0.5. A typical test, No. 12 (a run without driers), is shown in Figure 11 illustrating this behavior. Although this is not in complete agreement with the results of the equilibrium analysis, it is relatively close. The maximum conversion occurs over a range of O/H values from 0.3 to 0.5, rather than only at a fixed value of 0.5. This again indicates the predominating influence of kinetic rather than equilibrium effects upon  $\text{CO}_2$  conversion.

#### Test Results - Nos. 13 to 14

The next group of two tests was run to determine the effect of operating without the pelleted catalyst. In previous tests the pellet catalyst was found to disintegrate at reaction temperature into a fine powder which was sometimes carried out of the reactor. It appeared desirable to eliminate this catalyst, if possible. Using the steel-wool catalyst throughout the reactor, but with the lower 6-inch section still at 700 to 750°C, and the upper 18 inches at 525 to 550°C, and with no driers in the system, the  $\text{CO}_2$  conversion rate was approximately 70% (350 cc/min) of the original Battelle rate with driers and pellet catalyst. Because the pellet catalyst seemed unsuitable for use at the desired reaction temperature, and because the conversion rate did not decrease significantly (a drop from 80% to 70% of original rate), the pellet catalyst was eliminated from subsequent tests.

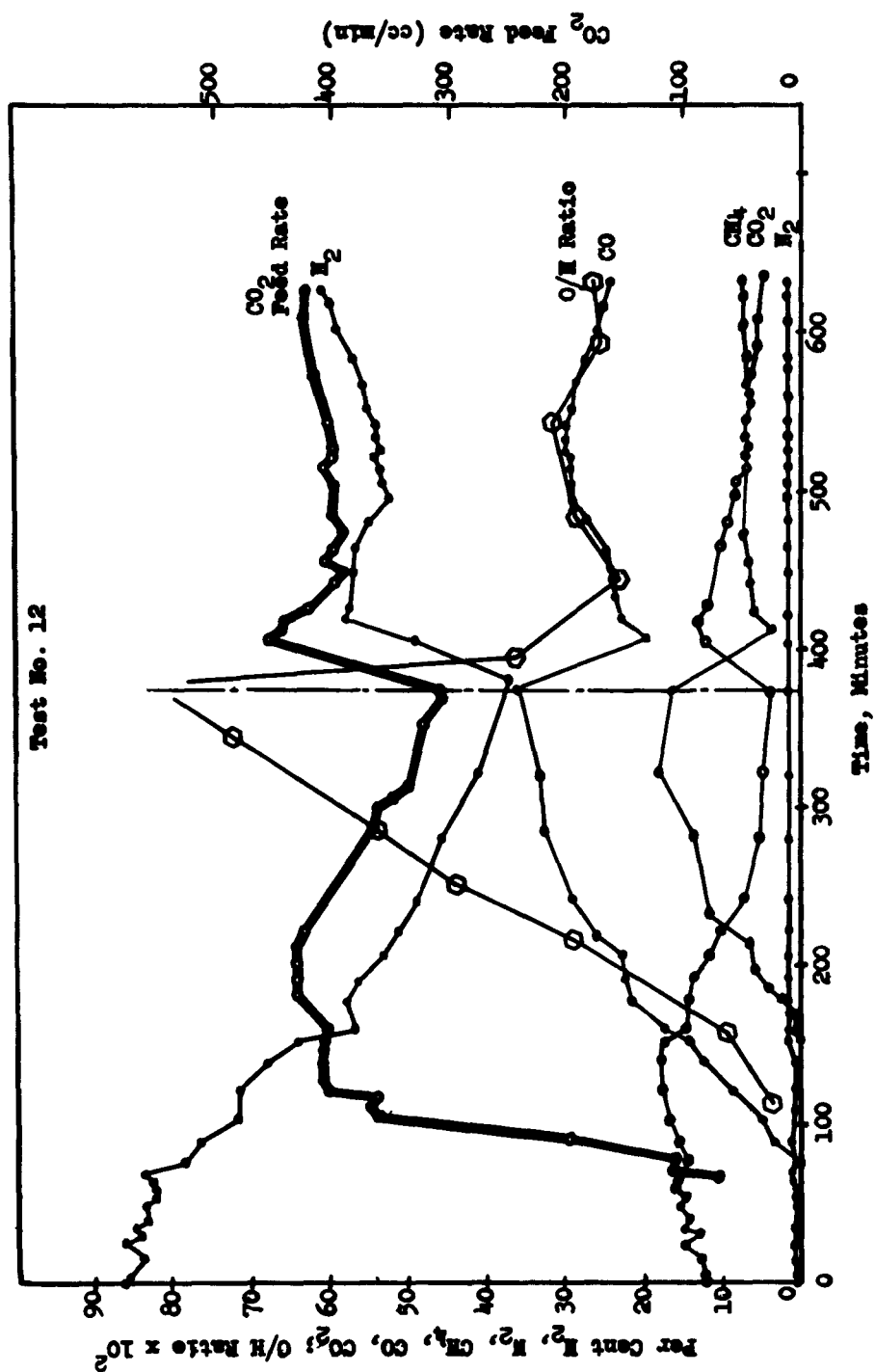


Figure 11  
EXPERIMENTAL TEST NO. 12, GRAPHICAL RESULTS

#### Test Results - Nos. 15 to 19

The next group of five tests was directed at determining the effect on CO<sub>2</sub> conversion rate of (1) raising the 525 to 550°C section of the reactor to 700° to 750°C, and (2) varying the point at which the feed is introduced in the reactor. Although the entire reactor was heated to an external temperature of approximately 725°C, the top six inches of the catalyst was at a lower temperature due to cooling by the inlet gas stream. The top of the catalyst was at 500°C and this temperature rose to 700°C within the first six inches. Under these conditions the CO<sub>2</sub> conversion rate increased to approximately 75% (375 cc/min) of the Battelle rate. The system was being operated at 9.0 psig, the original Battelle recycle rate of 0.67 cfm, and O/H ratio of approximately 0.40, and the feed was injected at a level six inches above the bottom of the steel-wool catalyst.

The feed was next injected directly in the inlet gas stream prior to entry into the reactor. With the system still at the same increased temperature level no measurable change could be noted in the CO<sub>2</sub> conversion rate. This is of importance because if the feed does not have to be injected into the catalyst directly, the overall reactor design may be considerably simplified.

#### Test Results - Nos. 20 to 23

The next group of four tests investigated the effects of raising the recycle rate to values greater than 0.67 scfm. The recycle rate was raised 1.45 cfm and the CO<sub>2</sub> conversion rate rose in almost direct proportion to 900 cc/min, or approximately 1.8 man capacity. The recycle rate was raised further for a short time to 2.40 scfm and the conversion rate rose in fairly close proportion to 1300 cc/min, or slightly over 2.6 man capacity. This recycle rate was sufficient to dislodge some carbon particles from within the catalyst-bed, and to cause subsequent plugging of the system. Small particles of steel-wool catalyst material were also dislodged from the catalyst-bed by the high flow rate.

#### Test Results - Nos. 24 to 26

Three additional tests were next run using carbon-steel screen material as a catalyst instead of steel-wool. These tests were run to determine (1) if screen material having the same surface area as the steel-wool would provide the same CO<sub>2</sub> conversion rate, (2) if screen material would retain its original configuration and not break into small particles due to reaction effects, and (3) whether carbon could be blown completely out of the reactor on a continuous basis at a sufficiently high recycle rate.

These tests indicated that the steel screen material catalyzed the conversion at the same rate as steel-wool. With a recycle rate of 1.12 scfm the CO<sub>2</sub> conversion rate was 700 cc/min, and at 1.82 scfm it was 1000 cc/min. During these tests the water condenser tubing clogged due to carbon build-up from previous runs and from a small amount of very fine carbon generated in these runs. This behavior indicated that carbon must not be allowed to enter the water condenser under any circumstances. A steel-wool filter was placed in the reactor outlet line, and a new condenser with a larger diameter gas line was installed. The additions eliminated further plugging.

The screen material retained its structural integrity for a total test period of ten hours. Screen wire diameter was 0.012 inches. Carbon collected



heavily on the screens, and only a very small amount was blown out of the catalyst, even at 1.82 scfm. Carbon was found to have formed almost completely in the cooler (500° to 700°C) end of the catalyst, with very little carbon in the hot (700° to 750°C) end.

#### Test Results - Nos. 27 to 32

The next group of six tests were run to observe the effects of automatic feed of H<sub>2</sub> and CO<sub>2</sub> gases.

These tests showed that both gases could be fed automatically, and that the maximum conversion rate under these conditions, with all other system variables held the same, was approximately 700 cc/min.

#### Test Results - Nos. 33 to 34

These tests were run to show the effects on reaction rate of operating at 2 psig instead of 9 psig.

The results of these tests indicated that changing the operating pressure level from 9 psig to 2 psig had a negligible effect on conversion rate.

### 3.5 Summary of Test Results

From the experimental tests conducted with the CO<sub>2</sub> reduction system the following results were determined:

- (a) The recycle gas composition should lie between an O/H ratio of 0.30 and 0.50 for maximum CO<sub>2</sub> conversion rates.
- (b) The steel catalyst must be adequately reduced with hydrogen for 24 hours at a minimum of 600°C.
- (c) The system can be operated without calcium sulfate driers for water removal, with only a 20% loss in conversion efficiency.
- (d) The system can be operated without a pelleted commercial catalyst in addition to the carbon-steel catalyst with no loss in efficiency.
- (e) CO<sub>2</sub> conversion rate increases by a factor of two for a 140°C increase in reaction temperature, in the range between 300°C and 750°C. Also, the CO<sub>2</sub> conversion rate increased when a greater portion of the reactor was raised to increased temperatures.
- (f) CO<sub>2</sub> and H<sub>2</sub> may be fed into the reactor along with inlet recycle gases, rather than at some point within the catalyst bed, with no loss in conversion efficiency.
- (g) The CO<sub>2</sub> conversion rate varies approximately directly with recycle flow rate.
- (h) Sufficiently high linear flow rates will slightly disturb carbon deposited in the catalyst bed.
- (i) Carbon-steel screen material of equivalent surface area with that of steel-wool used in previous experiments, will catalyze the reaction to give the same CO<sub>2</sub> conversion rate as with steel-wool. Screening, having a larger wire diameter than steel-wool strands, retains its structural integrity for a longer period.
- (j) The Battelle reactor can be operated continuously at a 2.6 man capacity with a sufficiently high recycle rate.

- (k) Carbon particles must not be allowed to enter the water condensing system. Moistened carbon agglomerates readily, and causes plugging of lines.
- (l) Feed gases may be fed automatically without any effect upon the conversion rate.
- (m) Changing the operating pressure level from 9 psig to 2 psig had a negligible effect on the conversion rate.

TABULATION OF EXPERIMENTAL TESTS

Test	Recycle SCFM	Temp °F	CO <sub>2</sub> Feed cc/min	CO <sub>2</sub> Converted <sup>a</sup> cc/min	O/H Ratio	Catalyst	Remarks
1-3	--	--	--	--	--	--	Shakedown runs. Charged reactor with CH <sub>4</sub> . Reduced catalyst with pure H <sub>2</sub> . Checked Chromatograph.
4	0.67	1000 <sup>b</sup> 1300 <sup>c</sup>	400	--	0.45	Steel- Wool + Pellets	First Battelle duplication. Reached only 80% of target rate. Ran without driers for short period. Rate decreased somewhat, but did not hold steady.
5	0.67	1000 <sup>b</sup>	410	--	0.50	S.W. and Pellets	Second Battelle duplication. Still 80% CO and CO <sub>2</sub> concentrations too high. Catalyst not completely reduced.
6	0.67	1000 <sup>b</sup> 1300 <sup>c</sup>	0	--	--	S.W. and Pellets	Initial charge of pure CH <sub>4</sub> decomposed to H <sub>2</sub> and C in presence of carbon from previous runs. Pressure rise prevented feed. Charge 80% H <sub>2</sub> , 20% CH <sub>4</sub> .
7	0.67	1000 <sup>b</sup> 1300 <sup>c</sup>	430	--	0.60	S.W. and Pellets	Third Battelle duplication. Still 80% CO and CO <sub>2</sub> again too high.
8	0.0	1000 <sup>b</sup> 1300 <sup>c</sup>	--	--	--	--	Filled reactor with CO <sub>2</sub> initially CO <sub>2</sub> began immediately to decompose to CO. Tabulated composition change. No run possible due to continuing change in pressure.
9	0.67	1000 <sup>b</sup> 1300 <sup>c</sup>	530	520	0.4-0.5	S.W. and Pellets	Fourth Battelle duplication. Successfully reached target rate. CO <sub>2</sub> build-up minimized.

Table of Experimental Tests (Cont'd)

Test	Recycle SCFM	Temp °F	CO <sub>2</sub> Feed cc/min	CO <sub>2</sub> Converted <sup>a</sup> cc/min	O/H Ratio	Catalyst	Remarks
10	0.67	775 <sup>b</sup> 1100 <sup>c</sup>	230	--	0.35-0.45	S.W. and Pellets	Checked effect of lower reaction temperature. CO <sub>2</sub> conversion decreased with decreasing temperature.
	0.67	600 <sup>b</sup>	95	--	0.30-0.50	S.W. and Pellets	
11	0.67	1000 <sup>b</sup> 1300 <sup>c</sup>	530	515	0.30	S.W. and Pellets	Maximum rate maintained with O/H ratio less than 0.50.
12	0.67	1000 <sup>b</sup> 1300 <sup>c</sup>	430	410	0.30-0.50	S.W. and Pellets	Operated system without driers, using ethylene-glycol cooled condenser to remove water formed in reaction. Decreased conversion by approximately 19%.
13	0.67	1000 <sup>b</sup> 1300 <sup>c</sup>	400	395	0.40-0.50	Steel- Wool	Operated without driers and without pellet catalyst. Decreased conversion by approximately 24%. Loss of 5% due to elimination of pellets. Driers and pellet catalyst will be eliminated in future tests.
14	0.67	1000 <sup>b</sup> 1300 <sup>c</sup>	410	400	0.40-0.50	Steel- Wool	Duplication of Run #13 to verify that catalyst was completely prepared and adequately catalyzing the reaction. Decreased by 23%. Verification satisfied.
15	0.76	1000 <sup>b</sup>	390	365	0.55-0.60	Steel- Wool	Raised recycle rate with extra pump. Conversion rate was lower than expected, due to O/H ratio being over 0.50.

Table of Experimental Tests (Cont'd)

Test	Recycle SCFM	Temp °F	CO <sub>2</sub> Feed cc/min	CO <sub>2</sub> Converted <sup>a</sup> cc/min	O/H Ratio	Catalyst	Remarks
16	0.67	1025 <sup>b</sup>	390	386	0.35	Steel- Wool	Normal recycle rate restored. Lower end of reactor raised to 1400°F. Rate appeared to fall off, even with O/H ratio in correct range.
17	0.67	1025 <sup>b</sup> 1300 <sup>c</sup>	295	290	0.15-20	Steel- Wool	O/H ratio lowered. Rate is below normal. System also developed a leak in feed valve, with resultant high nitrogen build-up, also causing rate to be lower.
18	0.55	1000 <sup>b</sup> 1025 <sup>b</sup> 1300 <sup>c</sup>	315	310	0.30-0.40	Steel- Wool	Recycle rate decreased by minor clogging of pump. Raised temperature of middle section of reactor from 1025 to 1250°F. Rate increased approximately 15%.
	0.55	1000 <sup>b</sup> 1250 <sup>b</sup> 1300 <sup>c</sup>	275	370	0.30-0.45	Steel- Wool	
19	0.55	1200 <sup>b</sup>	380	375	0.40-0.45	Steel- Wool	Changed inlet point of feed CO <sub>2</sub> and H <sub>2</sub> from 6 inches above catalyst bottom to inlet recycle gas line. No change in CO <sub>2</sub> conversion rate.

Table of Experimental Tests (Cont'd)

Test	Recycle SCFM	Temp °F	CO <sub>2</sub> Feed cc/min	CO <sub>2</sub> Converted <sup>a</sup> cc/min	O/H Ratio	Catalyst	Remarks
20	1.45	1000 <sup>b</sup> 1250 <sup>c</sup> 1300 <sup>c</sup>	940	910	0.40	Steel- Wool	Sliding-vane pump substituted for two diaphragm pumps used up to this point. Raised recycle rate. Vane pump used in all future tests.
21	2.40	1000 <sup>b</sup> 1250 <sup>c</sup> 1300 <sup>c</sup>	1230	--	0.10	Steel- Wool	Raised recycle rate again. System ran for approximately five minutes then clogged. Reached approximately 2-1/2 mm capacity.
22	2.30 to 1.23	1000 <sup>b</sup> 1250 <sup>c</sup> 1300 <sup>c</sup>	1050 to 570	--	0.30-0.45	Steel- Wool	Attempted run at high recycle rate again after cleaning system of carbon deposits from Run #21, and installing new carbon-free catalyst bed. Rates gradually fell off as carbon deposited and was blown out to plug up system again.
23	0.80	1000 <sup>b</sup> 1250 <sup>c</sup> 1300 <sup>c</sup>	--	--	--	Steel Screen (same surface area as with steel- wool)	Substituted 1" squares of 30 x 30 mesh, 0.012" diam. wire screen for steel-wool in top portion of reactor, with stainless steel-wool in bottom portion, to determine if carbon formed could be blown from screens to collect in steel-wool. Recycle flow stopped after four minutes, due to final plugging of condenser with carbon. No data taken.

Table of Experimental Tests (Cont'd)

Test	Recycle SCM	Temp °F	CO <sub>2</sub> Feed cc/min	CO <sub>2</sub> Converted <sup>a</sup> cc/min	O/H Ratio	Catalyst	Remarks
24	1.12	1000 <sup>b</sup> 1250 <sup>b</sup> 1300 <sup>c</sup>	400	--	0.10	Steel Screen	Replaced condenser with new condenser having larger diameter tubing. Added filter (heated to prevent condensation in filter) at inlet to condenser. Water immediately collected in condenser but did not drain properly. Recycle rate fell to zero within thirty minutes. No data.
25	1.12	1000 <sup>b</sup> 1250 <sup>b</sup> 1300 <sup>c</sup>	705	700	0.10-1.00	Steel Screen	Corrected condenser draining. Conversion rate is in proportion to recycle rate. Only very small amount of carbon being blown out of reactor and collected in filter. O/H ratio ranged from 0.10 to 1.00 and maximum rate occurred only between 0.25 and 0.50.
26	1.82	1000 <sup>b</sup> 1250 <sup>b</sup> 1300 <sup>c</sup>	1010	1000	0.20-0.50	Steel Screen	Raised recycle rate. Conversion rose proportionately. Still only small amount of carbon blown out. Raised recycle rate to 2.25 for short time but CO <sub>2</sub> -H <sub>2</sub> feed system could not deliver more than 1350 cc/min (2.6 man capacity). Reactor will deliver this capacity.
27	1.5	1300 <sup>c</sup>	400	400	0.30	Steel Screens	H <sub>2</sub> fed automatically by system total pressure regulator CO <sub>2</sub> fed manually. First attempt at separate feeding of H <sub>2</sub> and CO <sub>2</sub> . Operated satisfactorily.
28	1.5	1300 <sup>c</sup>	0-2000 (Intermittent)	750 (Average)	0.30	Steel Screens	H <sub>2</sub> fed automatically. CO <sub>2</sub> fed manually and intermittently to simulate adding CO <sub>2</sub> with automatic control system. Composition was measured with CO <sub>2</sub> sensor, and maintained by manual control of feed at predetermined level, approximating 7-9% of total gases as CO <sub>2</sub> .

Table of Experimental Tests (Cont'd.)

Test	Recycle SCFM	Temp °F	CO <sub>2</sub> Feed cc/min	CO <sub>2</sub> Converted <sup>a</sup> cc/min	O/N Ratio	Catalyst	Remarks
29	1.5	1300 <sup>c</sup>	700	690	0.30	Steel Screens	H <sub>2</sub> fed automatically. CO <sub>2</sub> fed manually at constant rate. 700 cc/min appears to be maximum capacity.
30	1.5	1300 <sup>c</sup>	750	700	0.30	Steel Screens	Same as Run No. 29. Verification.
31	1.5	1300 <sup>c</sup>	950	600	0.30	Steel Screens	CO <sub>2</sub> feed rate was increased to above rates in Runs 29 and 30 but water formation rate did not verify higher conversion rate. Re-checked CO <sub>2</sub> feed meter.
32	1.5	1300 <sup>c</sup>	630	630	0.30	Steel Screens	Verification that 700 cc/min is approximate capacity under conditions shown.
33	1.75	1300 <sup>c</sup>	750	700	0.25	Steel Screens	Operating Pressure was lowered from 9 psig to 2 psig. H <sub>2</sub> fed automatically and CO <sub>2</sub> manually. 700 cc/min conversion was reached.
34 (Final Test)	1.75	1300 <sup>c</sup>	950	900	0.25	Steel Screens	Duplicate of Run #33. Maximum conversion capacity was reached at 900-950 cc/min.

a. As measured by water collected

b. Upper 18 inches of reactor

c. Lower 6 inches of reactor



## SECTION 4

### ENGINEERING MODEL

#### 4.1 Design Requirements

In the CO<sub>2</sub> conversion system a number of basic requirements governed the arrangement and size of the system. These requirements were:

- (a) The CO<sub>2</sub> conversion rate must be 1500 cc/min, capable of supporting three men.
- (b) The catalyst should be easily replaceable, and its compartment or container readily cleaned.
- (c) The carbon formed in the reactor must be removed in a simple, efficient manner for storage or disposal.
- (d) The recycle gas flow rate should be optimized.
- (e) The power requirements should be a minimum.
- (f) The reactor must operate under the influence of weightlessness; and also in a range from 0 to 1-g of force, and should be capable of withstanding 15-g force.
- (g) The reactor should be as simple, compact and lightweight as possible, and should have a long life.

#### 4.2 Overall System and Flow Diagrams

The preliminary design of the CO<sub>2</sub> reduction system was composed of a reactor and carbon collector, a counter-current heat-exchanger water-condenser, a water separator, a recycle gas pump, and the CO<sub>2</sub> and hydrogen feed subsystem with overall system controls and instrumentation. Visual indicators were included for verifying proper system operation. These components, with the exception of the CO<sub>2</sub>-H<sub>2</sub> feed subsystem, are shown in Figure 12.

In the engineering model, all of these components, except the heat exchanger-water condenser, were constructed according to the preliminary design. The heat exchanger-water condenser construction was changed due to difficulties encountered in actual fabrication. Details of this change are described under paragraph 4.4.

A drawing of the assembled engineering model is shown in Figure 13. The arrangement and packaging of the components differs somewhat from the preliminary design, but in essence is the same as shown in Figure 12.

A block-type flow diagram is shown in Figure 14, illustrating the major components of the system and pressures, temperatures and composition at various points in the system. In essence a mixture of CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, and CO gases is continuously circulated in and out of the reactor in a closed loop. Water formed by the reaction of CO<sub>2</sub> and H<sub>2</sub> is continually removed and CO<sub>2</sub> and H<sub>2</sub> which have reacted are continually replaced. Carbon formed by the same reaction either (a) remains in the catalyst where the reaction takes place, and is removed when the catalyst is removed, or (b) is blown free from the catalyst section and into the carbon collector for periodic removal by blow-down with excess hydrogen gas. A pictorial type flow diagram showing the actual path of the gases in each component of the system is illustrated in Figure 15.



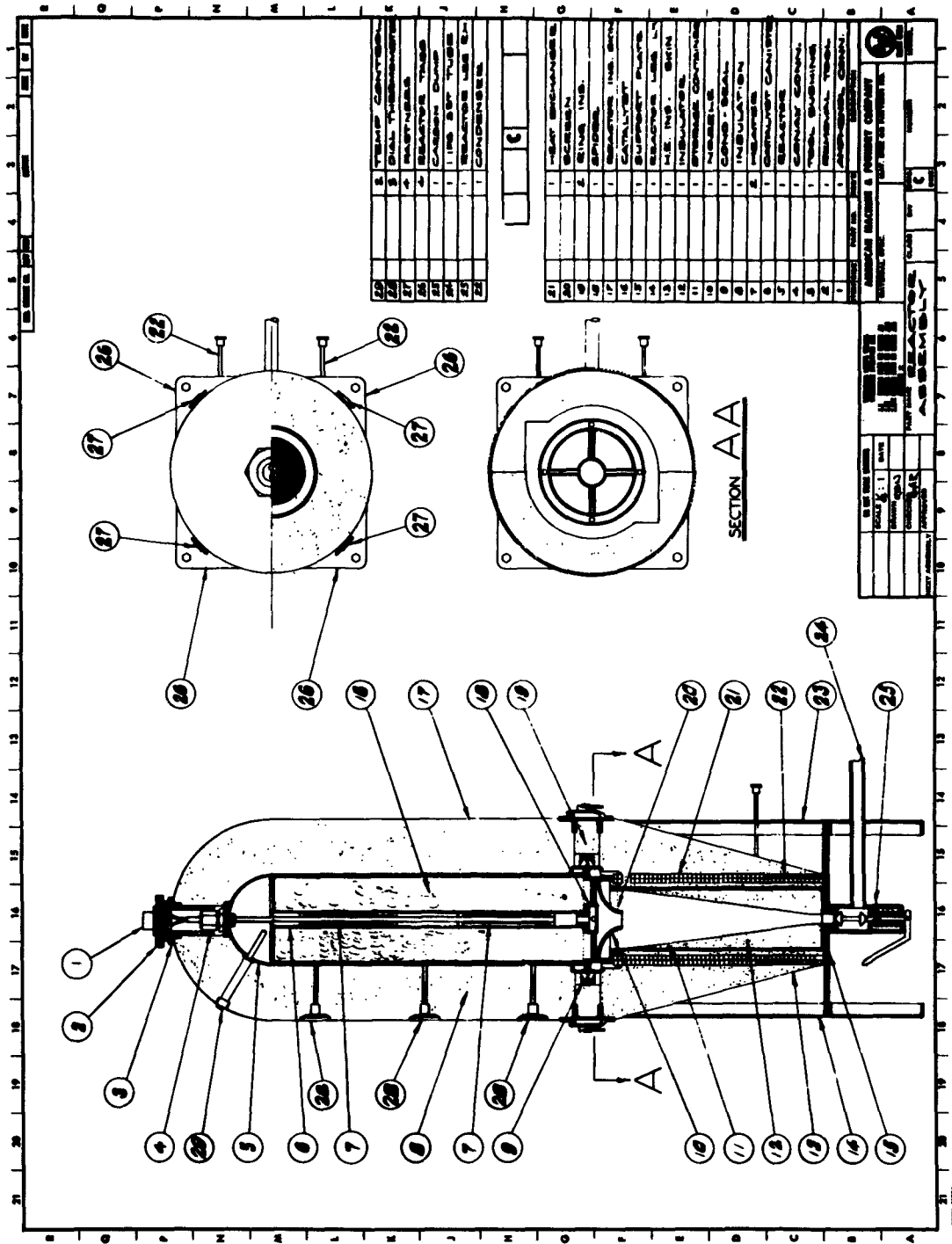


Figure 13  
REACTOR ASSEMBLY, PRELIMINARY DESIGN

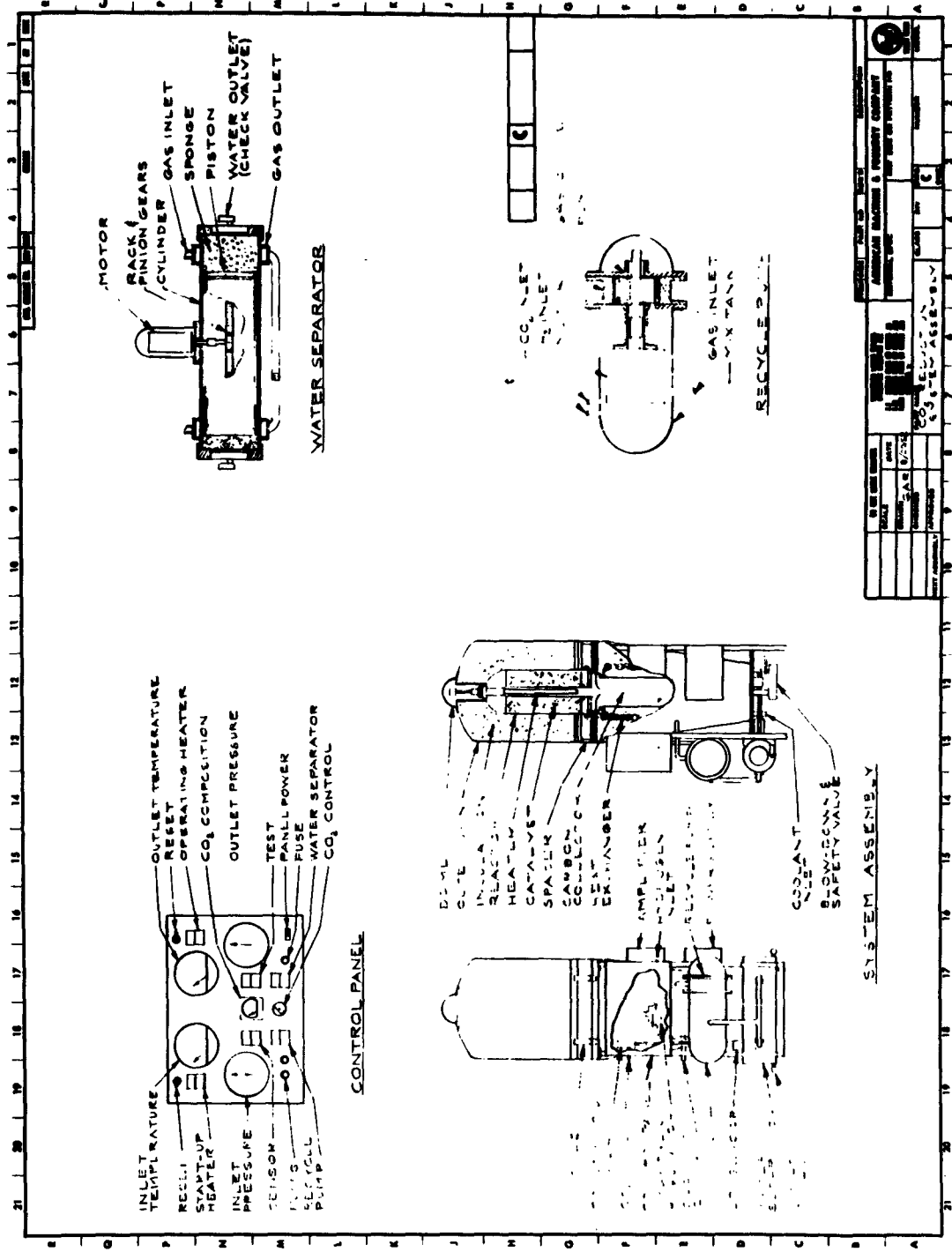


Figure 14  
CO<sub>2</sub> REDUCTION SYSTEM ASSEMBLY, FINAL DESIGN

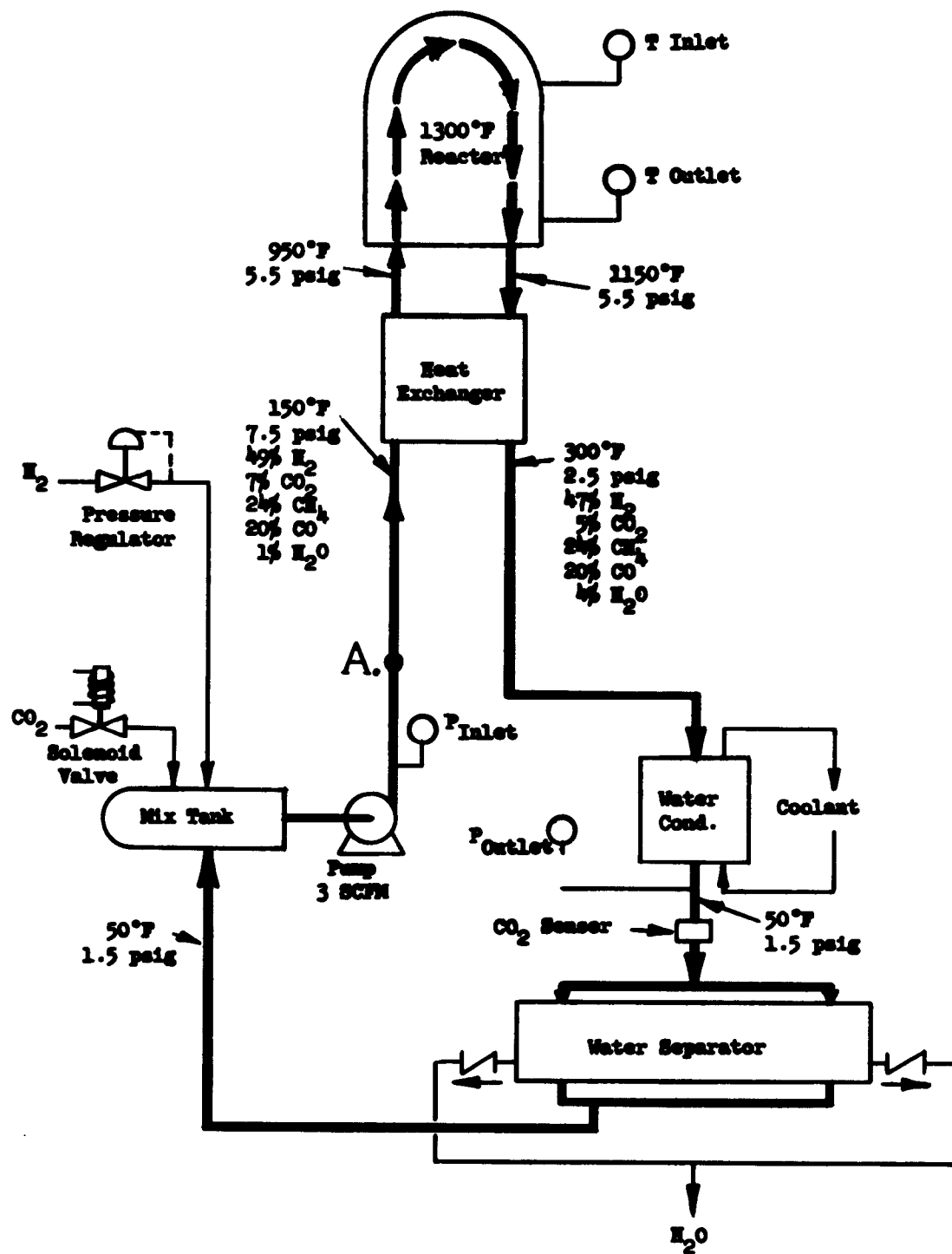


Figure 15  
CO<sub>2</sub> REDUCTION PROCESS BLOCK FLOW DIAGRAM

Starting at Point A on either diagram the mixture of gases enters the inlet side (annulus) of the counter-current heat-exchanger at approximately 100°F and 7.5 psig, at a flow rate slightly over 3 scfm. The composition by volume of these gases is 45-50%  $H_2$ , 5-7%  $CO_2$ , 35-40%  $CH_4$ , and 0-15% CO. Some water vapor is present, approximately 0.5 to 1.0% by volume, corresponding to the outlet composition of the water-saturated gas stream leaving the water condenser.

The gas mixture leaves the heat exchanger and enters the reactor at approximately 950°F and 5.5 psig. Within a central riser inlet tube the gas is heated further by an electric heater to 1300°F. The gases reverse flow direction and pass through a large annulus containing iron catalyst wherein the reaction to form water and carbon takes place. By the time the gases have passed through the catalyst the temperature has dropped to 1150°F. These reacted gases then enter the outlet side (center tube) of the heat exchanger at this temperature, and still at 5.5 psig.

The gases leave the heat exchanger and enter the water condenser at approximately 200°F and 2.5 psig. Sufficient cooling of the gases occurs to condense 75% of the water present in the gas stream. The gases, with entrained water droplets, leave the condenser at 50°F and 1.5 psig, and enter the water-separator.

In the water separator the entrained water droplets are trapped in sponges, while the gases pass through for further recycling. The gases leaving the water separator pass into a mixing tank which is mounted integrally with the recycle pump.

A carbon dioxide detector cell is located in the recycle gas piping leaving the condenser. The signal from the detector is used to operate a feed valve which adds  $CO_2$  to the gas stream entering the reactor.

The preliminary design called for a servo-operated valve, but this was changed in the engineering model to an ON-OFF type solenoid valve. The solenoid valve provided adequate flow control, and was more reliable and required simpler controls than a servo valve. The system total pressure is transmitted to a pressure regulator which controls the hydrogen feed supply and adds  $H_2$  to the gas stream entering the reactor.

Together these two subsystems add  $CO_2$  and  $H_2$  in the correct amounts to replace  $CO_2$  and  $H_2$  which reacted to form water and carbon. The complete gas mixture enters the pump at 50°-60°F and 1.5 psig, and leaves the pump at 150°F and 7.5 psig. This returns the loop to the original starting point A. A detailed description of each of the major components is given in the following paragraphs.

#### 4.3 Reactor and Carbon Collector

In the preliminary design it was assumed that carbon would be left undisturbed in the catalyst during  $CO_2$  reaction and that the carbon would be removed during cleaning of the system. Carbon could be removed together with the catalyst material when the volume capacity of the reactor is filled with carbon, and a new catalyst package could then be inserted in the reactor. As an alternate method, excess hydrogen gas could be blown through the catalyst at a high velocity to dislodge carbon from a rigid fixed catalyst configuration for disposal overboard through an appropriate valving system. Both of these methods

presume that carbon would collect and remain within the reactor during the reaction process.

Based on experimental measurements of the density of carbon formed in the reaction, the volume of carbon formed by three men in one day is 0.113 cubic feet. The length of a four-inch diameter reactor is 16 inches for a one-day operation, and 54 inches for three and one-half days. The length of a six-inch diameter reactor correspondingly is 7 inches for one day, and 24 inches for three and one-half days. The dimensions of a reactor for storage of carbon formed over periods longer than three and one-half days were found excessive and were not considered. The 6-inch diameter and 24-inch length were considered the more desirable combination of dimensions from insulation loss calculations. The preliminary design of the reactor proper is shown in detail in Figure 16.

In the engineering model the active conversion section of the carbon dioxide reactor consists of a thin-walled removable 5-3/4-inch diameter cylinder, 12 inches long, fitted to the inside of the main reactor body having approximately the same length. Although the preliminary design called for a 24-inch long reactor, both 12- and 24-inch sizes were constructed for comparison purposes during experimental testing. The shorter unit was found to be capable of delivering the desired conversion rate; the unit also was lighter and could be started up and heated by only a single heater. For these reasons the shorter unit with one heater was adapted for use in the engineering model.

The reactor section is filled with catalyst. An inlet tube one inch in diameter runs up the center of the catalyst zone, thus providing the inlet line for gases entering the reactor, and also providing the proper location for the 3/4-inch diameter heater element which heats the incoming gases. The resulting constricted flow past the heater element is necessary to provide the high linear flow velocity needed for adequate transfer of heat from the element to the inlet gases.

The catalyst cylinder is fitted with coarse screen material on both ends to form a canister for holding the catalyst material. The inlet gas tube is fitted with arms to center it within the canister, and may be disassembled to remove or replace catalyst material. The catalyst is iron in the form of a screen-like expanded metal approximately .02-inch thick cut in one-inch squares.

The canister fits into the main reactor body which measures six inches in diameter and approximately fifteen inches long from the top of the hemispherical end to the connection flange end. The top of the canister seals against a lip at the top of the reactor body by means of an asbestos gasket. This seal prevents recycled gases from passing between the walls of the canister and the reactor.

The lower end of the reactor body is fitted with one-half of a special aircraft-type flanged connection. This flange mates with the other half of the flanged connection attached to the upper end of the carbon collector. The two flanges are drawn together by a ring-type V-clamp fitted with two bolt-and-nut assemblies for drawing up on the clamp. A special stainless-steel gasket ring between the flanges seals the connection.

The reactor is insulated with a four-inch thick layer of an asbestos-magnesia type of soft felted insulation material. The insulation is protected from external damage by a 0.032" thick aluminum skin suspended from the reactor

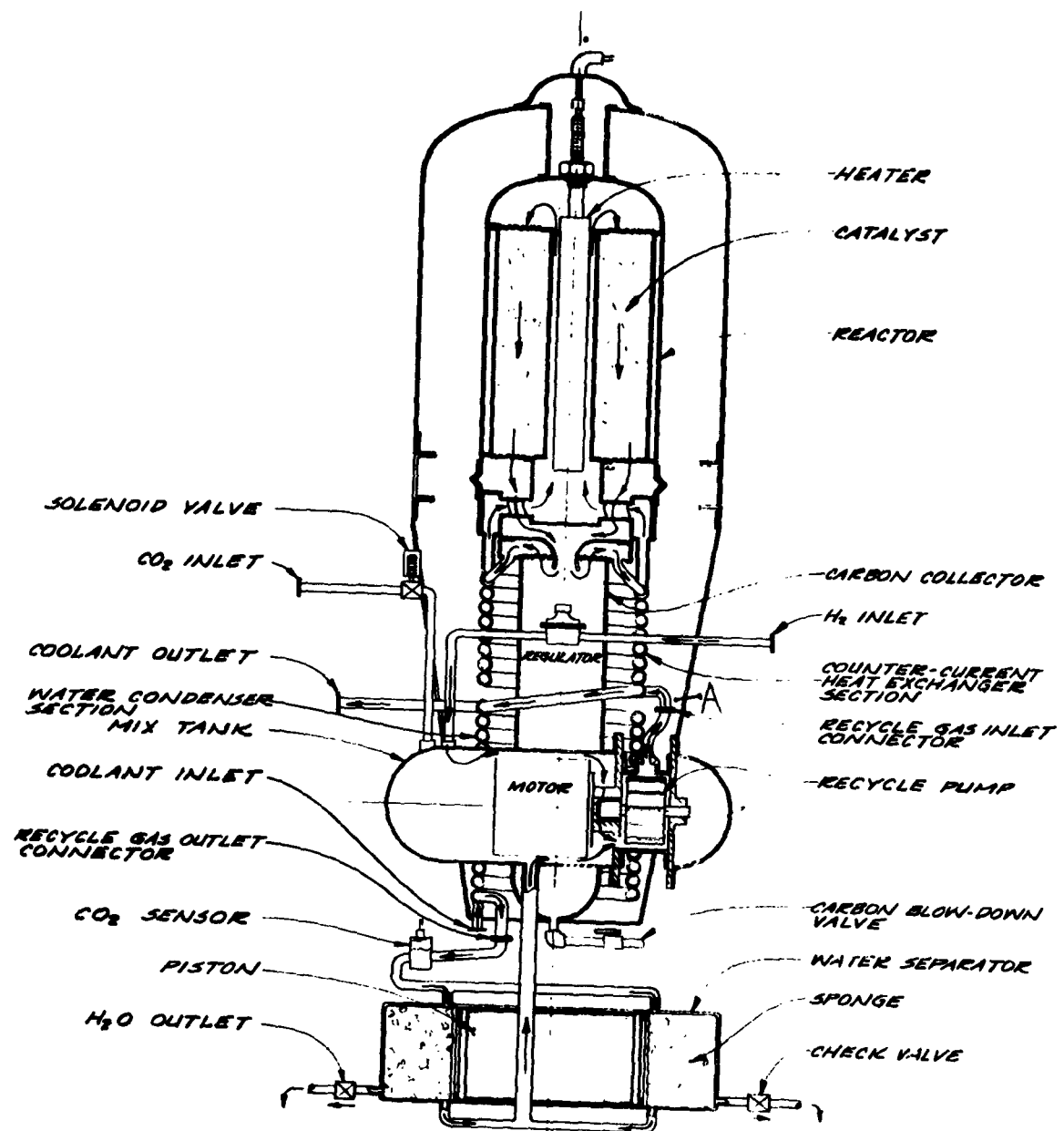


Figure 16  
CO<sub>2</sub> REDUCTION PROCESS PICTORIAL FLOW DIAGRAM



body. At the flanged end of the reactor, the soft insulation is protected by a one-half-inch thick layer of hard concrete-asbestos type insulation material.

At the hemispherical end of the outer aluminum-skin is a small aluminum dome which houses an electrical disconnect coupling for the two leads providing power to the heater element. This coupling allows removal of the heater element without the need for cutting the heater leads.

The carbon collector body is a four-inch diameter stainless steel one-eighth-inch wall tube, twenty inches in length. The upper inlet end is fitted with a nozzle plate which physically lies directly beneath the outlet of the reactor. Four outlet ports lying just below the nozzle plate are provided in the wall of the carbon collector, leading to the outlet gas side of the counter-current heat exchanger. A stainless steel wool filter is provided just beneath the nozzle plate at the outlet port holes to prevent passage of carbon into the heat-exchanger.

Four inlet ports are provided in the wall of the carbon collector, just above and outside the outer edge of the nozzle plate. The inlet ports lead in from the inlet gas side of the heat-exchanger to a distributor manifold mounted at the top of the carbon-collector. The distributor manifold butts directly up against the bottom end of the central inlet gas tube in the reactor canister. The nozzle, manifold, and central inlet tube are sealed with asbestos gaskets to their respective mating surfaces.

The bottom end of the carbon collector is hemispherical, and is fitted with an outlet pipe pointing down. The outlet pipe leads to a 30 psig safety relief-valve with an override handle for periodic removal of carbon by blow-down with hydrogen gas.

At the flanged end the carbon collector is wrapped with a four-inch thick layer of soft insulation, with the upper end protected by a one-half inch thick layer of hard asbestos-concrete insulation. The four-inch thick layer extends down for approximately six inches and then tapers uniformly down to a one-inch thick layer at the bottom of the carbon collector.

The outer-surface of the soft insulation is protected by a 0.032" thick aluminum skin. This skin also extends across and is bolted to the bottom end of the collector.

The bottom end of the carbon collector is mounted on a support frame of aluminum angles and plates. The angle supports extend up to the top of the aluminum skin around the collector, and tie into an aluminum ring welded to the top edge of the skin. The reactor is connected to the carbon-collector and is supported by means of the previously described flange and clamp assembly.

#### 4.4 Heat Exchanger-Water Condenser

To minimize the power requirements necessary for operating the CO<sub>2</sub> reduction system an efficient optimum design heat exchanger is required to recover the heat energy in the hot gases leaving the reactor for transfer to cold gases entering the reactor. A counter-current exchanger was selected since this type provides the maximum final temperature of incoming gases, and minimum final temperature of effluent gases.

A mathematical model was developed on the basis of a square-tube exchanger so that an optimum design for the exchanger could be determined. A bundle of

four square tubes was selected since in this configuration the walls of the square tubes act as heat-transfer fins and provide an effectively greater heat-transfer area. From the mathematical analysis and a weight penalty trade-off for power requirements, a program was developed for a study with the IBM 1620 computer at the MRD Division.

The complete heat-exchanger optimization is shown under Item IV in the Appendix. The results of the study showed that a bundle of four, 5/16-inch square tubes at 92% effectiveness provided the optimum design. The coiled diameter was chosen to correspond to the six-inch reactor diameter. The height of coil required was found to be approximately ten inches, with a coil weight of 8 pounds.

Although this type of exchanger was shown theoretically to be highly appropriate for the CO<sub>2</sub> reduction system, problems encountered in final fabrication prevented its ultimate use. Special extrusion dies, or special welding apparatus would have been required for fabrication, and an excessive amount of time would have been required for providing either of these special fabricating systems. Consequently, the square tube configuration was not utilized in the final engineering model.

The round-tube concentric counter-current heat exchanger was relatively similar to the square-tube design in many of its heat transfer characteristics and could be wrapped readily in the required helical form.

Consequently, in the engineering model, the heat-exchanger consists of a 3/8-inch O.D. copper tube. This tube assembly is wrapped in a close-wound helix, 8-inch O.D. by 6-1/2-inch I.D., and approximately 12-inches high. The inlet gases flow up through the annulus, and outlet gases flow down through the central tube.

The helix is located around the upper 12 inches of the carbon collector, in the center-section of the soft insulation. The inlet connection to the annulus is on the right-front side of the insulation skin, approximately nine inches above bottom. The inlet gas annulus terminates in four connection tubes leading from the outlet ports also at the top end of the carbon collector. The outlet gas line passes out of the heat exchanger coil and into the water condenser coil.

The water condenser is exactly similar to the heat exchanger, i.e., 3/8-inch I.D. and 3/4-inch O.D. tubes, wrapped in an 8-inch O.D. by 6-1/2-inch I.D. helix. The helix is approximately 7 inches high and is located directly below the heat exchanger around the lower 7 inches of the carbon collector within the soft insulation. The outlet gases flow down and out through the central tube which passes through the bottom support plate under the carbon collector. A liquid coolant such as water or ethylene glycol-water solution passes up through the annulus counter-current to gas flow. The inlet to the coolant line is under the bottom support plate and the outlet is on the left side of the carbon-collector insulation skin, approximately 8 inches above bottom.

#### 4.5 Water Separator

The water formed in the CO<sub>2</sub> reduction is the desired end product, and has to be continuously removed from the reactor outlet gas stream. A water separator has been designed to meet the need for continuous water removal without penalizing or restricting gas flow.

The water-separator consists of a double-end, 4-inch diameter aluminum piston moving back and forth within a horizontal closed 14-inch long aluminum cylinder, alternately compressing and releasing a 3-1/2-inch thick water-absorbing sponge at each end of the cylinder. The piston is driven from one end to the other by a brass rack and pinion gear train. The pinion gear is mounted on the drive shaft of 100V A.C. electric motor, with rotation reversed automatically by an electrical switching circuit. The motor and switching circuit are mounted on the outside rear wall of the cylinder, within a gasketed bullet-shaped aluminum housing.

The ends of the cylinder are fitted with gasketed removable caps. Removal of these caps provides direct access to the absorbing sponges, and to the piston and gear-train drive.

Inlet gas connections to each sponge are mounted on the rear wall of the cylinder. The outlet connections are on the front wall, and are joined by a header tube with a connection line leading to the recycle pump.

The removable caps on each end of the cylinder are fitted with check valves to prevent gas outflow during water absorption. The valves release water to a collection tank when the piston has closed off the gas inlet and is compressing the water out of the absorption sponge. The collection tank is vented to the system at any point between the outlet from the condenser to the recycle pump inlet.

The sponge material is polyurethane foam with a coarseness of 30 pores per inch. This type of sponge is water absorbent, and is flexible whether wet or dry.

#### 4.6 Recycle Pump

In the continuous operation of the CO<sub>2</sub> reduction system a reliable, efficient, non-leaking, and long-life means for recycling the gases through the reactor is required. Experience with positive displacement diaphragm pumps indicated that these pumps do not leak but that their reliability and life are not adequate for recycle requirements. Small particles of entrained carbon plugged check valves in these pumps and effectively prevented pumping. Blower fans were found to be inefficient, mainly because they could not develop enough positive pressure to overcome the pressure drop in the system, which, although small, was not negligible.

A positive-displacement sliding-vane pump operated reliably and efficiently, and did not leak. This pump is of simple construction with large, unobstructed, inlet and outlet parts, and operates effectively against the pressure drop in the system. On the basis of actual experience and comparison with diaphragm pumps and a blower fan, the vane-pump was selected for the preliminary design and was used in the engineering model. The pump consists of a rotor and sliding graphite vanes, which revolve in a cast-iron housing with aluminum end plates. The vanes run dry and do not require a lubricant.

Spun aluminum cups are mounted on the end plates with O-rings to prevent any outleakage of gas along the pump shaft. One of the end cups is elongated to serve as a mixing tank for combining inlet feed gases with recycled gases. An inlet port has been cut in the corresponding end plate for entrance of the gas mixture. The normal pump inlet has been sealed with a plug.

A 220-volt, three-phase 1700 RPM drive motor is mounted within the enlarged cup, and is coupled directly to the pump.

The incoming cup, and the incoming feed gases enter on the rear side. The gas mixture leaves the pump through the normal pump outlet which points upward.

The actual pump rotor-housing is exposed to ambient temperatures to permit dissipation of the heat of compression and friction generated during operation. This amount of heat is not inconsiderable as evidenced by the rise in temperature of recycled gases from 70°F at the inlet to approximately 150°F at the outlet of the pump.

#### 4.7 Controls and Instrumentation

The variable controls in the CO<sub>2</sub> reduction system are the reaction temperature control, the hydrogen partial pressure control, and the carbon dioxide partial pressure control. The instrumentation components in the system are system inlet and outlet pressure gauges, reactor inlet and outlet temperature indicators, carbon dioxide composition indicator, heater element indication on-off switch and circuit breaker, recycle-pump indicating on-off switch and fuses, and water-separator indicating on-off switch and fuse.

The reaction temperature control, which operates the heater element, consists of a Fenwal bimetallic temperature-sensing switch, an electric relay, and an on-off switch and circuit breaker. The bimetallic switch is mounted inside the upper end of the reactor body, with the temperature sensing element positioned at the hottest point in the flowing gas stream at the outlet of the central riser tube in the catalyst canister. The switch is normally open, but when the temperature rises above the set-point the switch closes. The sensitivity span of the switch is approximately 30°F, and the range of the switch is from 300° to 1500°F. Since the system is required to act at maximum capacity the switch is set at 1300°F, the optimum operating temperature as determined experimentally. The operating set point is altered by a screw on the external end of the switch which protrudes through the aluminum insulation skin near the top left side of the reactor housing. Screwing in raises the set point. A protective cap over the setting screw is held in place by two small screws.

Because the system is operated at maximum conversion capacity the switch set-point need not be altered after initial setting. For this reason no provision was made for continual alteration of the set point with a control knob on the instrumentation-control panel, although this had been originally planned in the preliminary design.

In normal operation the reactor heater should be on at all times when the gas temperature at the top of the reactor is 1300°F or less, and off when the temperature exceeds 1300°F. The bimetallic switch is open at 1300°F or below so a normally closed relay activated the switch is used to supply power to the heater element. The relay is closed and supplied power to the heater at 1300°F or below, and is opened to cut off power above 1300°F. The heater relay is mounted in the upper control circuit box positioned on the right side of the system angle supports. A removable lead-cable connects the temperature switch to the relay. Another removable lead cable supplies power from the circuit box to the heater element connection under the dome at the top of the reactor insulation skin.

On the instrument panel the heater is turned on or off by means of a lighted indicating "On-Off" switch. All indicating on-off switches are

Minneapolis-Honeywell "Micro-Switches". Either the On or Off half of the switch is lit indicating the status of power supply to the heater circuit, but not necessarily that the heater itself is actually on or off, since this is controlled by the automatic bi-metallic switch. A manually re-set Klaxon Circuit-breaker is located on the instrument panel above the "On-Off" switch to protect the heater from over loading. The circuit-breaker is energized with the switch in the right-hand position.

The reactor heater must not be turned on until the recycle gas pump has been started and gases are being circulated. Turning on the heater in a stagnant gas stream will result in burning out the heater element in a matter of ten or fifteen seconds.

Two temperature indicators are provided on the instrument panel. The "Inlet" temperature is the reactor wall temperature at the top of the canister where the gases enter the catalyst. The "Outlet" temperature is the reactor wall temperature at the bottom of the canister where gases exit from the catalyst bed.

These Lewis Co. ambient temperature-compensated indicators are millivolt meters calibrated in °F to read directly the output from Chromel-Alumel thermocouples attached to the reactor surfaces. At normal reaction temperatures of 1300°F inside the reactor, the "Inlet" reads 1200°-1225°F, and the "Outlet" reads 1075°-1100°F.

The hydrogen partial pressure control consists of a Bastian & Blessing diaphragm and spring type pressure regulator operated to total system pressure. This regulator senses the system pressure in the gas mixing tank on the inlet side of the recycle pump. The operating output range of the regulator is 1 to 5 psig, and the sensitivity span is 0.1 psi.

The required supply pressure to the regulator for a 1 to 5 psig output is a minimum of 8 psig, and maximum of 50 psig.

Two Aircraft Components, Inc., pressure indicators are provided on the instrument panel. The inlet pressure gauge indicates the system pressure at the inlet to the gas annulus of the heat-exchanger. The outlet pressure indicates the system pressure in the gas outlet line from the water-condenser. Both indicators are marked from 10" Hg to 50" Hg, absolute, which is equivalent to -10 psig to +10 psig.

The regulator is set at approximately 1.5 psig, (33" Hg) as indicated on the outlet pressure gauge when the recycle pump is running. This lower setting was chosen to simulate the operating pressure level which might exist aboard space craft.

In operation the regulator allows hydrogen gas flow at pressures below 1.5 psig. At pressures equal to or greater than this set-pressure the regulator closes completely and stops flow. The regulator allows flow at a varied rate based on the demand of the system to maintain the set pressure, and no metering or throttling valve is required in conjunction with the regulator.

The operating set-point is altered by a notched screw plate in the neck of the regulator. Screwing the plate down raises the set-point pressure. The top of the neck is protected by a removable cap.

The hydrogen regulator is just beneath the control panel. No provision is necessary on the control panel for continued adjustment of the operation pressure, since the reaction conversion rate is not greatly affected by pressure variation.

Although the hydrogen pressure regulator actually senses the system total pressure rather than hydrogen partial pressure, it does effectively control the hydrogen partial pressure. In system operation the CO<sub>2</sub> control system directly senses CO<sub>2</sub> partial pressure and maintains it at a pre-determined level. The remaining partial pressures of gases in the system can be raised or lowered only by raising or lowering the total system pressure. Under operating equilibrium conditions the partial pressures of gases other than CO<sub>2</sub> and H<sub>2</sub> remain constant. Therefore controlling the system total pressure controls the hydrogen partial pressure.

The carbon dioxide partial pressure control consists of a Beckman Co. carbon dioxide sensor, an electronic amplifier and power supply, a composition set-point control knob, a composition indicator with a zeroing control knob, and a Skinner Co. electric solenoid valve.

The carbon dioxide sensor is located in the outlet gas line between the heat-exchanger terminus and the inlet to the water separator. The sensor consists of a glass-electrode cell sensitive to the hydrogen-ion concentration of a jelly-like solution suspended in a gas-permeable membrane around the electrode. Passage of carbon dioxide through the membrane, either into or out of the jelly-like solution, changes the hydrogen-ion concentration which in turn causes a change in the output of the glass-electrode cell. The output from the electrode cell is utilized to indicate and control the carbon dioxide concentration. The sensor is connected by a removable cable to a jack and two plug-in receptacles at the top of the amplifier circuit housing. This housing and the power supply housing are mounted on the right side of the system support frame.

The sensor output signal is electronically amplified and compared with an adjustable reference signal. The reference signal set-point is controlled by the CO<sub>2</sub> control knob on the instrumentation panel. If the cell output signal is lower than the reference point, indicating a CO<sub>2</sub> concentration lower than required, a circuit operates to open a solenoid valve which admits carbon dioxide into the system. Conversely, if the output signal is higher than the reference point, indicating excess CO<sub>2</sub>, the circuit does not operate and the unenergized solenoid valve remains closed. Excess carbon dioxide is automatically consumed during reactor operation, thus lowering the concentration to the required level.

The carbon dioxide concentration is shown on the CO<sub>2</sub> composition indicator on the instrumentation panel. The meter is calibrated from 0.0 to 2.0 units. The passage of the meter needle from 0.0 through 2.0 signifies a change in CO<sub>2</sub> concentration from 0.0 to 5.6% by volume at 1.5 psig and 50°F at the sensor. To signify concentrations above 5.6% the needle should be re-set to 0.0 immediately upon reaching 2.0. The second sweep from 0.0 through 1.0 signifies a concentration change from 5.6% to 36.0% CO<sub>2</sub>. The relation between the meter reading and the concentration is approximately logarithmic, and the calibration is as follows;

	Meter	CO <sub>2</sub> Vol. %
1st Sweep	0.0	0.0
	0.5	0.4
	1.0	0.9
	1.5	2.2
	1.7	3.2
	1.8	3.8
	1.9	4.8
	2.0-0.0	5.6
2nd Sweep	0.1	6.7
	0.2	8.1
	0.3	9.9
	0.4	12.0
	0.5	14.5
	0.6	17.2
	0.7	22.2
	0.8	25.0
	0.9	30.0
	1.0	36.0

Initially when no CO<sub>2</sub> is present the CO<sub>2</sub> composition indicator must be zeroed by means of a small zeroing control knob on the upper end of the amplifier circuit housing. The same knob is used to reset the needle from 2.0 to 0.0 to utilize the second sweep range.

In normal reactor operation the CO<sub>2</sub> concentration at the sensor in the outlet gas line is approximately 5% by volume. Once the CO<sub>2</sub> composition indicator has been zeroed a concentration corresponding to 5% CO<sub>2</sub> should be simulated on the indicator by turning the zeroing control knob. The indicator reading should be approximately 1.9 as noted from the calibration table.

With the indicator reading 1.9 the CO<sub>2</sub> control knob below the indicator is slowly rotated to open the solenoid CO<sub>2</sub> feed valve. Rotation should stop as soon as the valve clicks open, thus correctly positioning the control knob at the desired set-point of 1.0. In general the set-point is positioned before CO<sub>2</sub> is introduced into the system. However, the set-point may be raised or lowered at any time, including during operation, by rotating the control knob.

The sensitivity span of the composition control is approximately 0.05 units on the indicator. Thus the CO<sub>2</sub> solenoid valve will remain open until the reading rises to 1.95; the valve will then close and remain closed until the reading falls to 1.85.

The pressure of CO<sub>2</sub> to the solenoid valve should be approximately 3 psi above the system outlet pressure. The CO<sub>2</sub> feed to the solenoid valve should be throttled to slightly over 3-man capacity, approximately 1600 cc/min. These feed conditions are necessary to overcome the 3.0 psi drop across the solenoid at 1600 cc/min of CO<sub>2</sub>, and to supply sufficient CO<sub>2</sub> to maintain the optimum CO<sub>2</sub> concentration of 5% by volume in the outlet gas stream.

The recycle pump is operated by a lighted indicating "On-Off" switch on the lower left side of the instrument panel. The switch is a triple-pole, double throw unit, since the recycle pump motor requires three-phase, 220-volt power. The switch is tied directly to the three-phase, 220-volt incoming power supply to the instrument panel. Two phases of the power are fused to protect

the motor from overloading. The fuse holders are located on the panel. In the event of a fuse blow-out a small neon light in the end of the fuse holder lights up denoting the blow-out.

The indicating "On-Off" lights in the switch show the position of the throw bar. These lights however are powered by the 110-volt line to the panel, rather than by the 220-volt supply.

The water-separator is also operated by a lighted indicating "On-Off" switch on the lower right side of the panel. The circuit to the drive motor is protected with one fuse to prevent motor overload. The fuse is located on the panel front, and in the event of fuse blow-out a small neon light in the fuse holder lights up. The indicating on-off lights show whether power is supplied to the water-separator drive motor.

Both 110-volt single-phase and 220-volt three-phase power are supplied to the instrument panel. The entire system, with the exception of the recycle pump, operates on 110-volt power which is fed through a manually re-set circuit breaker switch at the lower right corner of the panel.

#### 4.8 System Assembly and Preparation for Operation

The carbon dioxide reduction system has been designed to allow system operation and maintenance with a minimum of assembly and repair steps.

##### Reactor-Carbon Collector Assembly

The major step in assembly of the unit requires joining the reactor upper section to the carbon-collector lower section. The mating ends of each section are fitted with special stainless steel grooved flanges. A machined stainless steel gasket fits in the grooved surfaces to seal the flanges.

The flanges are drawn together by a circular clamp with a vee-shaped cross-section. The clamp is divided into two halves, and the halves are fitted with draw-bolts at the junctions of the halves, for tightening the clamp.

In preparation for assembly the flange surfaces must be wiped clean. Very fine steel wool may be used if necessary. It is essential that the corners of the grooves be clean and smooth.

The circular clamp should be laid in place around the flange on the carbon collector. The gasket should next be positioned on the flange groove, making sure the gasket contour matches the contour of the flange face.

The bottom end of the inlet tube in the center of the reactor canister terminates in a flat ring surface fitted with four locating pins. An asbestos gasket, the same size as the ring, fits over the four pins, flush against the ring face. This gasket seals the canister inlet tube to the inlet gas manifold at the top of the carbon collector. The gasket should be pushed over the four pins prior to joining the reactor to the carbon-collector.

With the asbestos gasket in place, the reactor is carefully lowered onto the carbon collector. The four locating pins must be fitted into four mating holes in a matching ring at the top of the gas manifold on the carbon collector. When the reactor is finally in place the space between the mating flanges should be less than 1/32 inch.



The circular clamp is tightened around the flanges, and the stainless steel gasket is compressed and actually cold-worked to completely seal the flange-joint. The clamp is tightened by drawing-up on the two bolts joining the clamp halves. The clamp should be tapped with a hammer while tightening, and each bolt tightened to between 160- and 200-inch-pounds of torque.

Two insulated spacers fit in the open two-inch space between the assembled reactor and carbon collector. These spacers are held in place by four latch assemblies attached to the reactor and carbon collector insulation skins. The latch assemblies draw the insulation skins together slightly, and provide additional rigidity to the system support structure.

#### Heater Replacement

In the event that the heater element requires replacement, the heater may be removed without disassembly of any other part of the system. The heater element is accessible through the top of the reactor insulation skin.

The power supply cable to the heater may be disconnected from the protective dome by unscrewing the electrical connector. The dome should be loosened by removing the screws holding it to the insulation skin. A special two-wire connector lies under the dome inside a layer of soft insulation. The dome and soft insulation have to be carefully raised to expose the connector. Once exposed, the ceramic-insulated heater lead wires should be disconnected from the connector. The dome, insulation, and connector may then be completely detached from the reactor top.

The heater mounting assembly is now exposed, and the special removal wrench may be inserted in place. The heater mounting assembly is removed by unscrewing with the removal wrench. The mounting assembly is sealed to the threaded coupling in the reactor body by a special asbestos and stainless steel gasket, which will be removed along with the complete heater assembly.

Once the heater assembly is removed, a new replacement assembly, including a new asbestos and stainless steel gasket may be inserted. The male threads on the assembly must be coated with a lubricant such as Swagelok Co. "Silver Goop" capable of withstanding at least 1800°F for prolonged periods. The lubricant is essential to preventing galling and freezing of the mounting threads.

After the heater assembly has been replaced, the Teflon connector, insulation, and dome are reassembled, and the power supply cable is re-connected.

#### Catalyst Replacement

Removal of the catalyst requires disassembly of the reactor from the carbon collector. This is accomplished by reversal of the procedure described under "Reactor-Carbon Collector Assembly".

Once the reactor has been detached the catalyst canister may be removed from the reactor body. (In the engineering model additional special thermocouples were provided which probe into the catalyst material, passing through both the reactor and canister walls. These thermocouples must be removed before the canister will slide out of the reactor. The thermocouples may be removed by loosening special fittings and nut assemblies at the outer surface of the aluminum insulation skin).

After the canister has been removed from the reactor, the internal support assembly should be removed by unscrewing four small cap screws on the bottom rim of the canister. This will free all of the catalyst, inlet tube, support arms, and both bottom and top screens from the canister wall. The catalyst may then be removed for disposal.

In preparation for replacement with new catalyst the top screen is removed from the top support arms. The tube, support arms, and bottom screen are then replaced in the canister wall and screwed in place with four cap screws. New catalyst is added to the canister through the top until filled. The top screen is then re-wired to the top support arms. The canister is ready for replacement in the reactor.

Before replacing the canister a new asbestos gasket should be inserted to fit between the rim at the top inside of the reactor and the top rim of the canister. With this gasket in place the canister may be re-inserted. (The canister in the engineering model should be rotated to line up the thermocouple holes in the canister wall with the matching holes in the reactor wall. The thermocouples should be re-inserted into the catalyst, and the fittings and nuts on the outside of the insulation skin should be re-tightened).

#### Leak Testing

Prior to operation of the system all connections, joints, seals, valves, fittings, and flanges, should be tested for leaks. As a preliminary to actual leak testing a manometer should be connected into the system, preferably anywhere between the gas outlet from the condenser and the inlet to the recycle pump.

When the system has been completely connected and all probable leak sources have been visually and mechanically checked, the pressure should be raised to approximately 10 psig. The pressure loss rate as indicated by the manometer should not exceed 2 mm. (0.2 cm) per minute. If the pressure loss rate is equal to or lower than this rate no further leak testing is required since this is the residual leak rate for the system as determined experimentally.

If the pressure loss rate is greater than 2 mm/min, the system should be pressurized with Freon gas and tested for leaks with either an alcohol-flame detector, or an electronic halogen detector. After leaks have been found the pressure loss rate should be equal to or less than 2 mm/min.

After leak testing the system should be purged with pure hydrogen gas in preparation for system operation.

#### Catalyst Preparation

When new catalyst has been added to the system, and after the system has been satisfactorily leak-tested, a 24-hour period is required to condition the catalyst.

Prior to heating during conditioning, the system should be purged with hydrogen. The hydrogen should feed through the hydrogen pressure regulator set at 1.5 psig (33" Hg) on the outlet pressure gauge. This is necessary to replace hydrogen which is lost through leakage. The system pressure must be held above atmospheric; otherwise a vacuum might be created on the inlet side of the recycled pump and air could leak into the system. If possible the gas

composition should be tested with a chromatographic analysis to insure that no oxygen is present. If oxygen is present it must be purged out, since this creates an explosive hazard, and also if heated will oxidize and weaken the copper heat-exchanger.

Once the system is purged with hydrogen, the recycle pump should be turned on. Adequate recycling flow-rate is indicated if the differential pressure with hydrogen is approximately 8" Hg (4psig). (Note: This differential is not the same as when the equilibrium gas mixture is being recycled.) The OUTLET pressure gauge should read 33" Hg (1.5 psig) and the INLET gauge 41" Hg (5.5 psig). If this differential is not achieved the recycle pump is malfunctioning or the flow system is plugged, either of which require correction before proceeding further.

The ethylene-glycol water coolant should now be circulated through the condenser. It is essential that the coolant be circulated to prevent 200°F gases leaving the heat-exchanger from passing uncooled through the condenser and over the carbon dioxide sensor in the gas outlet line from the condenser. The maximum allowable operating temperature for the sensor is 104°F. The coolant must be circulated whenever the system heater is turned on.

Up to this point the 110-volt power switch should be off. Also, the CO<sub>2</sub> supply to the CO<sub>2</sub> solenoid feed valve should be closed off manually to prevent inflow of CO<sub>2</sub> due to opening of the solenoid valve. The 110-volt power switch for the panel may now be turned on. With the recycle pump running properly, the heater element may be switched on by actuating the circuit-breaker button and the ON-OFF switch.

From this point on the system will automatically heat the reactor and catalyst to 1300°F, and hydrogen will be continually circulated over the catalyst. This circulation of hydrogen will condition the catalyst if carried on for 24 hours after the temperature reaches 1300°F.

When 1300°F is attained in the reactor the temperature INLET and OUTLET gauges should read 1220° and 1100°F, respectively.

#### 4.9 System Operation

In preparing for system operation, assuming the system does not leak, that the reactor is cold, and that the catalyst already has been conditioned, the system should be purged with pure electrolytic grade hydrogen (not natural gas extracted). All power to the panel should be off. The gas composition should be checked with a chromatograph if possible, to determine that no nitrogen or oxygen is present. Nitrogen decreases the system conversion capacity, and oxygen presents an explosion hazard. The hydrogen pressure regulator should be set at 33" Hg (1.5 psi) on the OUTLET pressure gauge.

The liquid coolant to the condenser should be circulated and kept on at all times while the system is in operation. If the coolant stops the system should be shut down immediately to prevent damage to the CO<sub>2</sub> sensor from over heating.

After purging with hydrogen the recycle pump may be started. The pressure drop should be 8 inches of Hg, with the OUTLET and INLET pressure gauges reading 33" and 41" Hg absolute, respectively. If this differential is not achieved the recycle pump is malfunctioning or running backwards, or the recycle system is plugged. These conditions must be corrected before proceeding further.

The 110-volt power to the panel is still off and the CO<sub>2</sub> solenoid is closed. Preliminary to turning on the panel power the CO<sub>2</sub> supply to the solenoid valve should be closed off, since the solenoid valve will open when panel power is turned on, assuming the CO<sub>2</sub> control set-point has been previously adjusted to the proper level. (See following paragraphs for set-point adjustment).

The 110-volt power should next be turned on. With the recycle pump running the heater element may be turned on. The reactor will now automatically heat up to the 1300°F reaction temperature level.

While the system is being heated, the CO<sub>2</sub> control set-point should be adjusted if this has not been previously done. The CO<sub>2</sub> control system is ready for operation approximately one-half hour after the 110-volt power is turned on.

The proper set-point is at 1.9 on the composition gauge. This composition signal should be induced on the gauge by using the zero control knob on the top of the amplifier box at the side of the system support frame. The CO<sub>2</sub> composition knob on the panel should be rotated to the position at which the solenoid feed valve clicks on and off. The valve should be left on and open. The composition indication should be returned to 0.0 by means of the zero control knob. This completes the adjustment of the CO<sub>2</sub> set-point.

When the reactor has heated to 1300°F the system is ready for CO<sub>2</sub> feed to begin. At this point the CO<sub>2</sub> supply valve may be opened slightly. The supply line should be fitted with a rotameter calibrated between 0 and 3000 cc/min of CO<sub>2</sub>. The initial CO<sub>2</sub> feed rate should be between 200 and 300 cc/min. The water-separator should be switched on at this time.

The reaction rate will be low at first because no CH<sub>4</sub> is present, so the CO<sub>2</sub> feed rate must be held down. As the CH<sub>4</sub> concentration rises due to the reaction, the CO<sub>2</sub> conversion rate will increase and the CO<sub>2</sub> feed rate may be increased.

If the initial CO<sub>2</sub> feed rate is too high the system pressure may eventually exceed the setting of the hydrogen regulator and stop hydrogen feed for a short period before the CO<sub>2</sub> control system stops CO<sub>2</sub> feed. If this occurs the H<sub>2</sub> concentration may drop to a point where the reaction rate will be exceedingly low, and the system will require a considerable amount of time to allow the hydrogen level to rebuild to the proper value. For this reason the CO<sub>2</sub> feed should be carefully metered in so as not to exceed the system capacity.

If carbon is already present in the reactor from previous reactor operation, during warm-up, CH<sub>4</sub> will automatically be formed due to the reaction  $2H_2 + C = CH_4$ . Under these circumstances CO<sub>2</sub> may be fed initially into the reactor at a higher feed rate, in the vicinity of 100 to 1300 cc/min. This higher initial feed rate may be accomplished also if CH<sub>4</sub> is bled into the system up to a concentration of approximately 30% by volume. If this is done the concentrations of H<sub>2</sub> and CH<sub>4</sub> should be verified by chromatographic analysis before admitting CO<sub>2</sub> feed.

The CO<sub>2</sub> feed rate should be gradually increased to 1550-1600 cc/min (3.1-3.2 man capacity) as soon as possible. If this rate is exceeded the CO<sub>2</sub> composition will exceed the set-point level and the solenoid will close to stop the CO<sub>2</sub> feed. The system is now in complete automatic operation.

As verification of proper recycle pump operation the OUTLET and INLET pressure gauges should read 33" Hg (1.5 psig) and 45" Hg (7.5 psig). This pressure drop of 6 psi indicates a recycle rate of 3.0 to 3.5 SCFM. If this pressure drop is not attained the system will not be capable of continuously converting CO<sub>2</sub> at 3-man capacity.

The conversion capacity of the system should be verified by measuring the rate of water formation. If water is not forming and collecting the system is plugged at some point and will eventually stop the CO<sub>2</sub> feed since water is not being removed from the recycled gas stream.

The water formed should be measured at 15 to 20-minute intervals to the nearest 0.1 minute, and nearest cc, to determine the water formation rate. This rate for 3-man capacity is approximately 130 cc/min.

Under these operating conditions the system should be capable of running for 24 to 30 hours. This time is limited by the volume of carbon which can be built up and stored within the reactor without blow-down.

The following steps should be performed in sequence when the system is to be shut down:

- a. Stop CO<sub>2</sub> feed by shutting off the supply to the CO<sub>2</sub> solenoid valve. All of the CO<sub>2</sub> in the system will react with H<sub>2</sub> and eventually be completely consumed, leaving only H<sub>2</sub> and CH<sub>4</sub> in the recycle gas stream.
- b. When the CO<sub>2</sub> composition indicator returns to nearly 0.0 and remains there for five minutes all CO<sub>2</sub> may be assumed reacted. Turn off the system heater.
- c. The water separator should be left in operation for an additional 30 to 45 minutes if the system is to be permanently stopped. If the system is to be stopped only temporarily, the water separator may be stopped immediately after all CO<sub>2</sub> has been consumed.
- d. After stopping the water separator the panel 110-volt power should be turned off.
- e. The recycle pump may be stopped at this point. Leaving the pump on will facilitate cooling the system, but is not essential.
- f. The glycol cooling system should be turned off only after the system has cooled to below 150°-200°F as indicated on both INLET and OUTLET temperature indicators. This is necessary to prevent damage to the CO<sub>2</sub> sensor from over heating.

#### 4.10 Engineering Model Test Results

The engineering model of the carbon dioxide system was tested in two phases. The reactor and heat-exchanger condenser were initially tested separately without the final water separator, recycle pump and system controls. The object of the first phase was to determine the operating characteristics of the reactor proper and the effectiveness of the internal heating system, including both preheating from the heat-exchanger and final heating by the electrical heater element.

In the second phase of testing all system components were assembled and tested as a unit. In this phase the behavior of the recycle pump, water separator and system controls was observed under the demands of actual operation, rather than under simulated conditions for each component.

The first phase of testing consisted of test runs No. 1 through No. 7. Briefly these runs showed that the reactor would provide slightly in excess of the required 3-man conversion capacity, that the heat-exchanger worked well at over a 90% operating efficiency, that the internal heater element provided in excess of the needed heating capacity but that bare-wire design resulted in shorting due to carbon build-up, and that the system could be operated at the required conversion rate for at least 17 hours based on available carbon storage capacity within the catalyst. It was also found that the reactor operating temperature radically affects the conversion rate, since a drop from 1250°F to 1050°F lowered the rate from 3.1 to 0.8-man capacity.

The second phase of testing consisted of runs No. 8 through No. 10. These runs showed that the recycle pump and automatic system controls operated properly, that the reaction proceeded as well at outlet pressures of 1.5 psig as at 5.8 psig, that a sheathed heater element did not short out, that the water-separator required re-design, and that the system could be run continuously for 21 hours at the required conversion rate using about 80% of the available carbon storage volume within the catalyst. These runs also showed that no carbon could be blown out of the catalyst into the carbon-collector even at recycle rates as high as 3.5 SCFM.

A listing of each experimental test is shown in the following table.

# ENGINEERING MODEL TESTS

Test Recycle Temp. °F		Press. psig		Conversion		Composition	Remarks
SCFM	IN - OUT	IN	OUT	CO <sub>2</sub> cc/min	% by Vol. °C		
1	2.1	1250-1140 <sup>a</sup>	12.0	6.0	900	CO <sub>2</sub> 4 H <sub>2</sub> 60 CH <sub>4</sub> 22 CO 15	Reduced catalyst with H <sub>2</sub> for 28 hours. In preparing heater element and testing, both copper and brass lead wires burned out. Pure nickel 14 ga. lead wires used successfully. Heater is 20 gauge Kanthal alloy, 15 ohm resistance, wound on coil open to gas flow. Catalyst is expanded iron metal cut in 1" squares. Heat exchanger plugged after 3 hours from copper oxide formed inside heat-exchanger during tests on heater element with air circulated in system. Cleaned oxide out with warm HCl solution. Removed small amount of loose carbon from catalyst and replaced cleaned catalyst in reactor. 53 cc H <sub>2</sub> O collected. Condenser outlet gas temperature 53°F.
2	2.3	1225-1150 <sup>a</sup>	8.7	5.8	1250	CO <sub>2</sub> 4 H <sub>2</sub> 50 CH <sub>4</sub> 22 CO 23	Used same catalyst from test No. 1 without further preparation with H <sub>2</sub> . Carbon dioxide could be fed in rapidly even at start-up, since the CH <sub>4</sub> level raised almost immediately to approximately 25% due to presence of small amount of carbon on catalyst which remained from Test No. 1. Feed rate up to 900 cc/min was easily and quickly reached in about 30 minutes. Raising rate to 1250 cc/min required almost 4 hours. This appears to be maximum reactor capacity under indicated operating conditions. Collected 727 cc H <sub>2</sub> O. Condenser gas temperature 52°F.
3	3.1	1235-1175 <sup>a</sup>	10.7	5.8	1650	CO <sub>2</sub> 4.5 H <sub>2</sub> 50 CH <sub>4</sub> 20 CO 25	Continued with same catalyst from No. 2 leaving carbon in place. Raised recycle rate. Conversion rate rose approximately in proportion to somewhat over 3-man capacity maximum for shown conditions. Collected 872 cc H <sub>2</sub> O. Power to heater is 650 watts. Condenser gas temperature 51°F.

# ENGINEERING MODEL TESTS (cont'd)

Test Recycle Temp. °F		Press. psig		Conversion		Composition	Remarks
SCFM	IN - OUT	IN	OUT	CO <sub>2</sub> cc/min	by Vol. °C		
4	3.1	1060-1010 <sup>a</sup>	10.3	6.2	400	CO <sub>2</sub> 0 H <sub>2</sub> 60 CH <sub>4</sub> 35 CO 0	Continued with same catalyst from No. 3, still allowing carbon to accumulate. The temperature level was approximately 175°F lower than previously. The maximum conversion rate reached was at best 400 cc/min, and this could be sustained only for 30 or 40 minutes at a time. 43 cc H <sub>2</sub> O formed.
5	2.3	--	8.8	5.8	---	--	The catalyst has not been changed since Run No. 2. The heater burned out while the system was being raised to the operating level. Examination showed that carbon build-up on exposed heater wires aborted the heater to the inlet gas-tube wall. No water formed.
6	2.7	1250-1185 <sup>a</sup>	9.3	5.7	1200	CO <sub>2</sub> 3 H <sub>2</sub> 47 CH <sub>4</sub> 38 CO 0	The heater again burned out after the system was in operation for over 4 hours. Failure was attributed to a physical fault in the element wire. The gas analysis also appeared uncertain since no CO was found present. 360 cc H <sub>2</sub> O collected. Condenser gas temperature 46°F.
7	3.5-2.5	1285-1170	4.3	1.3	1200 Max	CO <sub>2</sub> 2-6 H <sub>2</sub> 55 CH <sub>4</sub> 30 CO 0	Same catalyst from Runs 2-6, still undisturbed. Used final system recycle pump instead of laboratory pump. Also added CO <sub>2</sub> sensor and solenoid valve control, although actual CO <sub>2</sub> control was still manual. Heater switch was tested.
Recycle pump appeared to be malfunctioning and losing capacity. Gas temperature from pump outlet was 170°F. CO <sub>2</sub> control circuit malfunctioned and required correction. Heater switch performed correctly. System was operated at a lower pressure level without loss in conversion capacity. Gas analysis still shows no CO. 290 cc H <sub>2</sub> O collected.							
All carbon was removed at end of run, and catalyst was replaced. Total amount of H <sub>2</sub> O formed was equivalent to running at full 3-man capacity for 17 hours.							



# ENGINEERING MODEL TESTS (cont'd)

Test Recycle Temp. °F		Press. psig		Conversion		Composition		Remarks
SCFM	IN	OUT	IN	OUT	CO <sub>2</sub> cc/min	by Vol. °C		
8	1.9 <sup>d</sup>	1240-1125 <sup>a</sup>	3.6	1.7	--	CO <sub>2</sub> -- H <sub>2</sub> 60 CH <sub>4</sub> 40 CO --	New catalyst was added and reduced for 30 hours at 1200°F with H <sub>2</sub> . All components in final system were assembled and operated as a unit for first time. Recycle rate was still lower than desired, as determined from INLET and OUTLET pressures. CO <sub>2</sub> control appeared satisfactory. A total of 56 cc of water was formed at varied CO <sub>2</sub> feed rates. Condenser gas temperature 58°F.	
9	1.9 <sup>d</sup> (Est.)	1210-1090 <sup>a</sup>	4.0	2.0	--	CO <sub>2</sub> 6 H <sub>2</sub> 55 CH <sub>4</sub> 40 CO 0	Same catalyst from No. 8 was used. The system was operated under fully automatic control for first time. Recycle pump did not operate satisfactorily. Consequently the CO <sub>2</sub> conversion rate was extremely low. No water collected. The water separator did not function properly; the O-rings seized on an undercut section of cylinder and stopped piston travel. Water separator removed temporarily from system. Recycle pump also removed for inspection. The heater again burned out due to shorting from carbon build-up.	
10	3.0- 3.5 <sup>d</sup>	1300-1200 <sup>a</sup> 1220-1110 <sup>b</sup>	7.5	1.5	1600	CO <sub>2</sub> 4-5 H <sub>2</sub> 55 CH <sub>4</sub> 40 CO 0	Same catalyst from No. 8 and 9 re-used. Relatively no carbon was formed in these tests so start-up was very slow. Some extra CH <sub>4</sub> was bled in with H <sub>2</sub> feed to rapidly attain the 25-35% CH <sub>4</sub> concentration present at maximum feed rate conditions. Recycle rate was high after pump and plates were refinished and hard-coated. Also rotor was accurately shimmed in pump housing to prevent end-plate wear. Water separator was left out of system for re-design. A new design fully sheathed heater element was installed.  Under fully automatic control the system operated at over 3-man capacity for 21 hours continuously. Stopped at this point since recycle rate dropped. (Later examination showed pump bearing failure. Bearing was	

# ENGINEERING MODEL TESTS (cont'd)

Test Recycle Temp. °F		Press. psig		Conversion Composition		Remarks
SCFM	IN	OUT	IN	OUT	CO <sub>2</sub> cc/min % by Vol.	

10  
(cont'd)

replaced and pump re-operated properly.) Reactor was about 80% filled with carbon at end of run. None blown down into carbon collector, even at recycle rate of 3.5 SCFM. During 21-hour run a 10 psig relief valve vented to hood was placed in inlet line to reactor. Reactor outer wall temperatures read about 80°. 90°F lower on panel indicators than actual temperatures at same level inside reactor.

CO<sub>2</sub> control, heater element and control, H<sub>2</sub> control and all instrumentation operated properly. 2765 cc of H<sub>2</sub>O collected. Gas analysis still questionable since no CO was indicated, although higher temperatures may cause all CO to react completely to H<sub>2</sub>O.

- Temperatures Inside Reactor.
- Temperatures on Reactor Outer Surface.
- Composition in Outlet Gas Line from Condenser.
- Flow Estimated from Pressure Drop.

#### 4.11 Weight, Power, and Volume

In the preliminary design the total weight of the system was estimated at 160 lbs. In the engineering model the insulated reactor and heat exchanger condenser weighed approximately 25 lbs more than expected, and the support frame was 5 lbs higher than expected. The total weight of the engineering model is 190 pounds compiled as follows:

<u>Insulated Reactor and Heater</u>	35 lbs
<u>Canister Plus Catalyst</u>	4
<u>Insulated Carbon Collector</u>	52
<u>Heat Exchanger - Condenser</u>	21
<u>Recycle Pump</u>	21
<u>Water Separator</u>	11
<u>Feed System</u>	6
<u>Instrumentation and Controls</u>	14
<u>Piping</u>	6
<u>Support Frame</u>	<u>20</u>
	190 lbs Total

The average power requirement for the system in normal operation is 975 watts. This is approximately 350 watts higher than anticipated in the preliminary design and is due mainly to a heater requirement of 650 watts instead of an expected 300 watts.

<u>Heater</u>	650 watts
<u>Recycle Pump</u>	230
<u>Water Collector</u>	10
<u>Instrumentation and Control</u>	<u>85</u>
TOTAL	975 watts

The volume occupied by the total system is as follows:

$$4'-8" \text{ high} \times 1'-2" \text{ Deep} \times 1'-4" \text{ wide} = 6.5 \text{ ft}^3$$

#### 4.12 Summary on the Engineering Model

The engineering model consists of a reactor and carbon-collector, a heat exchanger water-condenser, a water-separator, a recycle pump, and system controls with instrumentation. Reaction temperature is 1300°F, pressure 5.5 psig, and recycle rate 3.0-3.5 SCFM.

The reactor is an insulated twelve-inch long by six-inch diameter tube filled with iron catalyst in the form of 1 inch-square screens. The catalyst requires preconditioning with pure hydrogen at 1300°F for twenty-four hours. The electrical heater inside the reactor is externally removable without disassembling the entire reactor. The carbon collector is an insulated twenty-inch long by four-inch diameter tube attached to the bottom of the reactor. A manual valve at the bottom of the collector permits periodic carbon removal. The reactor and carbon-collector are mounted on aluminum support angles and plates.

The heat-exchanger and water condenser are both counter-current, concentric tube heat transfer coils, wrapped in a continuous helix around the carbon-collector. The concentric tube configuration was used instead of a square tube bundle originally called for in the preliminary design due to difficulties in fabrication.

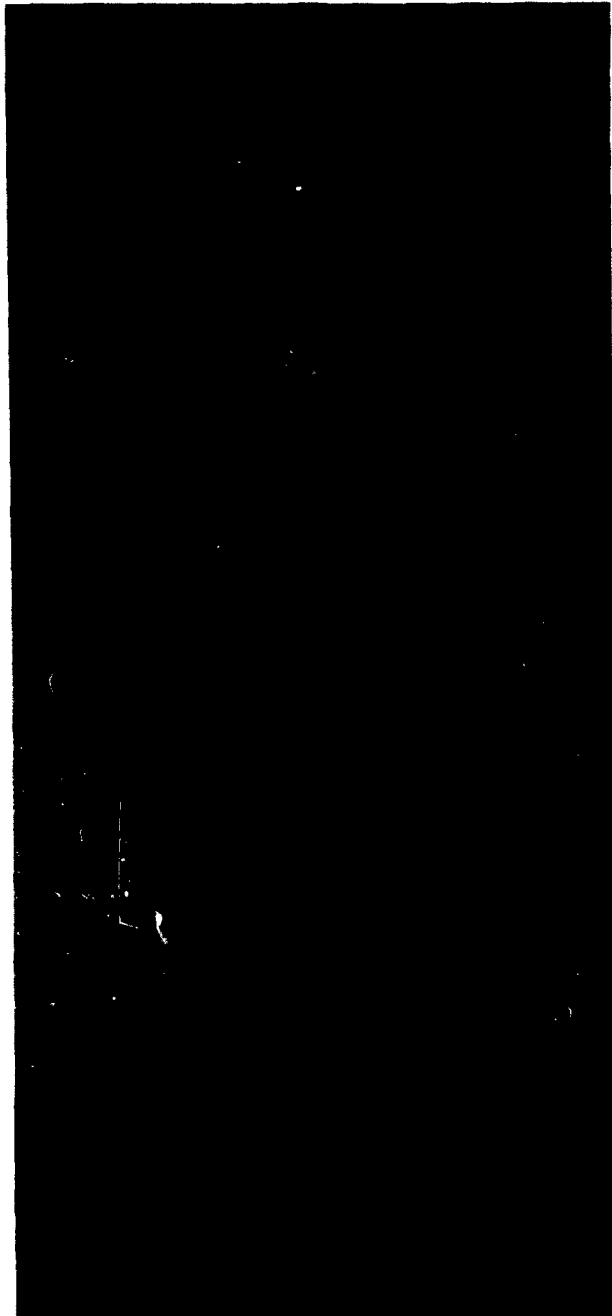
The water-separator is a 14-inch long by 4-inch diameter cylinder with a double-end piston alternately compressing and releasing a water-absorbing sponge at each end. The piston is moved back and forth by an electrical motor-driven rack and pinion gear assembly.

The recycle pump is an electric motor-driven sliding-vane positive displacement pump, enclosed in pressure-tight containers to prevent shaft leakage.

The system automatic controls are the reactor temperature control, the hydrogen feed and total system pressure control, and the carbon dioxide composition and feed control. The instrumentation components are system pressure gauges, reactor temperature indicators, gas composition indicator, and ON-OFF switches for the heater, separator, pump, and panel power.

Test results showed a  $\text{CO}_2$  conversion capacity in excess of the required capacity, with all components except the separator operating automatically and successfully. The continuous operating cycle is 24-30 hours, without carbon blow-down.

The system weighs 190 lbs, occupies 6.5 cubic feet, and requires an average of 975 watts of electrical power in normal operation. The engineering model is shown in Figure 17.



**Figure 17**  
**PHOTOGRAPH OF REDUCTION SYSTEM ENGINEERING MODEL**

## SECTION 5

### CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 Conclusions

Based on the results of the analytical, experimental and engineering model studies of the carbon dioxide reduction system, the following conclusions were developed:

(a) The engineering model will convert  $\text{CO}_2$  at a rate of 0.365 lb/hr which is 10% in excess of the design requirement for a 3-man capacity of 0.33 lb/hr.

(b) The recycle gas composition providing maximum  $\text{CO}_2$  conversion is approximately 5%  $\text{CO}_2$ , 50%  $\text{H}_2$ , 20%  $\text{CH}_4$ , and 25%  $\text{CO}$ , by volume at the reactor outlet.

(c) The engineering model reactor will accept  $\text{CO}_2$  immediately at the full conversion rate if the recycle gases contain 25-30%  $\text{CH}_4$ . This concentration may be induced by adding  $\text{CH}_4$  directly, or by the rapid reaction of carbon present in the reactor with  $\text{H}_2$  gas. If no  $\text{CH}_4$  is initially present the starting reaction rate will be approximately 20% of the full rate.

(d) The reaction  $\text{CO}_2 + 2\text{H}_2 = 2\text{H}_2\text{O} + \text{C}$  is predominantly influenced by kinetic effects rather than by chemical equilibrium effects. This is also apparent in that the operating O/H ratio is slightly over 0.20 rather than at 0.50 as predicted from chemical equilibrium concentrations alone. The reaction rate appeared to vary directly with the logarithm of the absolute temperature.

(e) Both carbon steel-wool and carbon-steel expanded metal screens were suitable catalysts. Stainless steel was found not to act as a catalyst.

(f) The iron catalyst must be preconditioned for reactor operation by reducing with  $\text{H}_2$  gas at 1200°-1300°F for 24 hours. After reducing, the catalyst may be left exposed to air or inert gas without loss of precondition effects. However, the preconditioned catalyst must be kept dry to prevent oxidation.

(g) The reactor temperature necessary for proper  $\text{CO}_2$  conversion rate is 1250° to 1300°F.

(h) The temperature of the outlet gas stream leaving the condenser must be 50°F or lower to provide 3-man capacity. Conversion rate will drop to zero if the condenser gas outlet temperature is 90°F or higher.

(i) The recycle flow rate required for 3-man capacity in the engineering model is between 3.0 and 3.5 SCFM.

(j) The  $\text{CO}_2$  and  $\text{H}_2$  feed gases may be fed to the reactor either separately or pre-mixed without effect on the conversion rate. The point at which the gases enter the reactor appeared to have no effect on the conversion rate.

(k) The system may be operated at 3-man capacity continuously for 24 to 30 hours without carbon blow-down or removal.

(l) The engineering model can be operated through start-up and continuous conversion with one electrical heater. The heater cycles in ON-OFF operation between 750 watts and no power, and is ON about 85% of the time for an average power consumption of 650 watts. Start-up time from ambient to reaction temperature (1300°F) requires approximately 5 hours using only the single internal heater. (See recommendations for discussion of shortened start-up time.)

(m) The concentric-tube counter-current type inlet-to-outlet-gas heat-exchanger performed with over 90% efficiency.

(n) During normal operation the catalyst arrangement did not allow dislodgement of carbon to the carbon collector. (See recommendations for discussion of methods for continuous carbon blow-down.)

(o) Total system pressure and hydrogen feed may be closely and automatically controlled by a pneumatic regulator.

(p) Carbon dioxide feed and composition level may be closely and automatically controlled by an electrolytic carbon dioxide sensor and an electronic control system.

(q) The system temperature can be automatically and closely controlled within 30°F by a bimetallic temperature-sensing switch.

(r) Actual reactor operating pressure may be varied between 2 and 10 psig without change in the CO<sub>2</sub> conversion rate.

(s) Proper system operation is adequately indicated visually by system inlet and outlet pressure gauges, reactor inlet and outlet temperatures, a CO<sub>2</sub> composition indicator, and system components operating ON-OFF lights.

(t) A reactor 5-3/4 inches in diameter by 12 inches long provides sufficient catalyst volume for the required 3-man conversion capacity.

## 5.2 Recommendations

Although the analytical, experimental, and engineering model studies led successfully to the development and fabrication of a system for converting carbon dioxide to water in excess of the required rate, further developments and improvements can be made to reduce the weight, size and required power for the overall system. Also the system could possibly be operated on a continuous basis without the need for periodic carbon removal if a different catalyst configuration were successful.

In light of the probable improvements which can be made in the system to provide continuous operation combined with lower system weight, size and power requirements, the following recommendations for a modified system are made:

(a) Various catalyst configurations, such as iron tubes or strips, should be investigated to determine if deposited carbon can be continually formed and blown free of the reactor, at the experimentally determined recycle rate for 3-man capacity. Investigation of this method of carbon removal is of primary importance, since successful continuous carbon removal could result in a greatly extended operating cycle and a very considerable reduction in the size of the reactor now used in the engineering model. (Present reactor dimensions were based primarily on carbon storing ability rather than on the volume of catalyst actually necessary to sustain the required conversion rate.) Size, weight, heat-loss and consequently power requirements, will be less if a smaller reactor is feasible.

(b) Additional investigation should be made to improve the heat-exchanger design. It may be possible to utilize a counter-current honey-comb type exchanger which would not only be lighter in weight but might have a considerably lower pressure drop than 6 psi. If the heat-exchanger pressure drop can be decreased, a smaller recycle pump weighing less and requiring less power could be substituted for the present pump.

(c) The possibility of utilizing a centrifugal type water separator should be investigated, to possibly eliminate the various mechanical difficulties encountered with the piston and sponge type separator.

(d) As an alternate to a mechanical or centrifugal water separator, a phosphorous pentoxide ( $P_2O_5$ ) combined water removal and electrolysis cell should be investigated. This type of cell would also eliminate the need for a water-condensing system in the recycle gas stream, since the outlet gases would no longer have to be cooled to 50°F. The system would thus require no ethylene glycol-water coolant.

(e) The long heating period required for system start-up could be considerably reduced by the use of an additional heater coil wrapped around the exterior surface of the reactor. An investigation should be made of the effectiveness of this type of auxiliary heater for start-up service, since the heater would not require gas circulation during heating to prevent heater burn-out. The heater could also serve as a redundant emergency operating heater.

(f) The use of a double-section internal-heater should be investigated to minimize power demand fluctuations, since the present heater draws 750 watts while on 85% of the time and zero watts while off the remaining 15% of the time. One section of the heater could be in continual operation at 600 watts with a 100-watt section in ON-OFF operation to supply the average 650-watt demand.



## SECTION 6

### REFERENCES

1. Foster, J. F., and McNulty, J. S., Study of a Carbon Dioxide Reduction System, Aeronautical Systems Division TR 61-388, August 1961.
2. Jacob, M., Heat Transfer, Volume II, Wiley & Sons, 1960.
3. Hougen, O. A., and Watson, K. M., Chemical Process Principles, Part Two, "Thermodynamics", Wiley & Sons, 1947.
4. Bird, R. B., Stewart, W. E., and Lightfoot, E. N., Transport Phenomena, J. Wiley & Sons, 1960.

## APPENDIX

### Item 1 - DEVELOPMENT OF EQUILIBRIUM CONSTANT, K, FROM FREE ENERGY AND ENTHALPY DATA

In deriving a statement for chemical equilibrium the following general equation may be written:



where C and D are reactants, R and S are the products, and c, d, r, and s are the number of moles of each, respectively, in a balanced stoichiometric reaction. The thermodynamic equilibrium constant, K, is defined in terms of the activities, a, of the reactants and products in equilibrium as follows:

$$K = \frac{(a_R^r)(a_S^s)}{(a_C^c)(a_D^d)}$$

This function of the equilibrium activities is a constant at a given temperature, depends only upon thermodynamic quantities, and is independent of kinetics or mechanisms of the reaction. The statement of the equilibrium relation allows the determination of the maximum yield of products that may be achieved from reactants at given concentrations.

In gaseous reactions, if the gases behave nearly as ideal gases their activities may be measured by partial pressures; also, if pure solids take part in the reaction, their activities are assumed constant, and equal to unity.

The equilibrium constant, K, is related to the Gibb's free-energy change in the standard state,  $\Delta G^\circ$ , according to the following formula:

$$-\frac{\Delta G^\circ}{T} = R \ln K$$

where T is the reaction temperature, and R the universal gas-constant. The quantity  $\Delta G^\circ/T$  may be evaluated from the following:

$$\frac{\Delta G^\circ}{T} = \sum \frac{G_T^\circ - H_0^\circ}{T} + \frac{\Delta H_{f0}^\circ}{T} \text{ Prod.} - \sum \frac{G_T^\circ - H_0^\circ}{T} + \frac{\Delta H_{f0}^\circ}{T} \text{ React.}$$

where,

$$\begin{aligned} G_T^\circ &= \text{standard Gibb's free-energy at temperature T} \\ H_0^\circ &= \text{enthalpy of the compound or element at } 0^\circ\text{K} \\ \Delta H_{f0}^\circ &= \text{standard heat of formation at } 0^\circ\text{K} \\ T &= \text{reaction temperature.} \end{aligned}$$

Tables of  $(G_T^\circ - H_0^\circ/T)$  versus temperature, and of  $\Delta H_{f0}^\circ$  for various elements and compounds are available and are based on data from the National Bureau of Standards.

A sample calculation of  $K_1$ , for the reaction at  $980^\circ\text{F}$  ( $800^\circ\text{K}$ );  
 $\text{CO}_2 + 2\text{H}_2 = 2\text{H}_2\text{O} + \text{C}$ , is as follows:

$$\frac{\Delta G^\circ}{T} = 2(-45.153) + 2 \frac{-57.108}{800} + (-2.164) + \frac{0.0}{800} - (-51.921) + \frac{-93.949}{800} - 2(-31.204) + \frac{0.0}{800}$$

$$R \ln K_1 = - \frac{\Delta G^\circ}{T} = +3.475$$

$$\therefore K_1 = 5.7473$$

## APPENDIX

### Item 2 - COMPILATION OF COMPUTER DATA AND GRAPHICAL REPRESENTATION OF EQUILIBRIUM CONCENTRATIONS

The five basic equations used in determining the equilibrium volume concentration,  $x$ , of the five gases  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ , and  $\text{CH}_4$  are as follows:

- $x_1, x_2, x_3, x_4, x_5$  - are concentrations at equilibrium of  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ , and  $\text{CH}_4$ , respectively
- $a_1, a_2, a_3, a_4, a_5$  - are initial (or inlet) concentrations, respectively
- $V$  - is the equilibrium volume
- $K_1, K_2, K_3$  - are the equilibrium constants for
- (1)  $\text{CO}_2 + 2\text{H}_2 = 2\text{H}_2\text{O} + \text{C}$
- (2)  $2\text{CO} = \text{CO}_2 + \text{C}$
- (3)  $\text{CH}_4 = 2\text{H}_2 + \text{C}$
- $\pi$  - is the reaction pressure.

1.  $x_1 + x_2 + x_3 + x_4 + x_5 = 1.0$
2.  $(2x_1 + x_3 + x_4)/2(x_2 + x_3 + 2x_5) = (2a_1 + a_3 + a_4)/2(a_2 + a_3 + 2a_5) = \text{O/H}$
3.  $K_1 = (x_3)^2/(x_2)^2(x_1)\pi$
4.  $K_2 = (x_4)^2\pi/x_1$
5.  $K_3 = x_5/(x_2)^2\pi$

The following constants were assigned:

- $C_4 = (K_1\pi)^{0.5}$
- $C_5 = (K_2/\pi)^{0.5}$
- $C_6 = K_3\pi$
- $R' = 1/(\text{O/H})$
- $C_7 = R'/2 + 1$
- $C_8 = R'/4 + 1$
5.  $x_5 = C_6(x_2)^2$
4.  $x_4 = C_5(x_1)^{0.5}$
3.  $x_3 = C_4(x_1)^{0.5}(x_2)$
2.  $x_2 = (1 - C_7x_1 - C_8C_5(x_1)^{0.5})/(1/2 + 1/2 C_7C_4(x_1)^{0.5})$
- $= \phi$
1.  $x_1 = 1 - \phi - C_4(x_1)^{0.5} \phi - C_5(x_1)^{0.5} - C_6(\phi)^2$

(All constants were used as real and positive numbers. All values of  $x$  were between 0 and 1.0.)

These five equations were then programmed for the IBM 1620 computer. For each temperature, pressure, and concentration, (as expressed in the  $\text{O/H}$  ratio, or as  $1/R'$ ) fixed values were assigned to the constants  $C_4$  through  $C_8$ . With this information the computer produced values for  $x_1$  through  $x_5$  for each set of conditions.

• The values of volume concentrations arrived at with this process are shown in the following table at the temperatures and pressure shown:

$T = 980^{\circ}\text{F}$  ( $800^{\circ}\text{K}$ );  $\pi = 9.0$  psig (1.6 atm. abs.)

$O/H$  varied from 0.0 to 10.0;  $K_1 = 5.7473$ ,  $K_2 = 0.01063$ ,  $K_3 = 1.3242$

$O/H$	$x_1$ ( $\text{CO}_2$ )	$x_2$ ( $\text{H}_2$ )	$x_3$ ( $\text{H}_2\text{O}$ )	$x_4$ ( $\text{CO}$ )	$x_5$ ( $\text{CH}_4$ )
0.0	.000	.491	.000	.000	.509
0.2	.075	.350	.292	.022	.260
0.3	.125	.310	.332	.029	.203
0.5	.231	.245	.357	.039	.127
0.67	.301	.210	.350	.045	.094
1.0	.410	.164	.318	.052	.057
2.0	.590	.098	.228	.063	.020
5.0	.762	.046	.118	.071	.004
10.0	.836	.023	.065	.075	.001
$\infty$	.924	.000	.000	.076	.000

The above data were used to plot volume concentrations versus  $O/H$  ratio on Figure 3, Section 2, Analytical Program.

# APPENDIX

## Item 3 - INSULATION OPTIMIZATION

$$Q = \frac{k_m A_m \Delta T}{\Delta x} = \text{Heat loss through insulation}$$

For a 27-inch cylinder with a 3-inch radius hemispherical end:

$$\frac{A_m}{\Delta x} = \frac{2\pi L(x_2 - x_1)}{(x_2 - x_1) \ln(x_2/x_1)} + \frac{2\pi x_2 x_1}{(x_2 - x_1)}$$

$$\begin{aligned} \Delta T &= T_R - T_S = 1400 - 125 = 1275^\circ\text{F} \\ T_R &= \text{Reaction temperature} = 1400^\circ\text{F} \\ T_S &= \text{Outer skin temperature} = 125^\circ\text{F} \\ k_m &= 0.02 \text{ Btu-ft/hr}^\circ\text{F-ft}^2 \\ L &= 27'' = 2.30 \text{ ft} \\ x_1 &= 3'' = 0.25 \text{ ft} \\ x_2 &= \text{Outer radius of insulation} \end{aligned}$$

Optimization is to show most favorable insulation thickness in light of one pound mass penalty for each six watts of power lost, with insulation weighing 20 lbs/ft<sup>3</sup>.

$$(a) \text{ Total Weight} = \text{Insulation Weight} + \text{Power Penalty Weight}$$

$$(b) \frac{Q}{k_m \Delta T 2\pi} = \frac{L}{\ln(x_2/x_1)} + \frac{x_2 x_1}{x_2 - x_1}$$

Solving (b) for  $x_2$  needed for various heat losses gives:

Heat Loss (watts)	Outer Radius (feet)	Insulation (inches) (lbs)	Power Penalty* (lbs)	Total (lbs)
100	.934	8.2 140.5	0.0	140.5
125	.707	5.5 77.4	4.2	81.7
150	.589	4.1 49.0	8.3	57.5
200	.471	2.7 26.8	16.7	43.5
225	.438	2.3 21.6	20.8	42.4
250	.414	2.0 18.0	25.0	43.0
300	.380	1.6 13.4	33.3	46.7

\* 100 watts of heat are supplied by the reaction at no power penalty. Penalties shown are for power needed over and above that supplied by reaction.

Optimum insulation thickness is 2.3 inches. The gas surrounding the insulation is assumed to be 100°F (maximum). This creates a 25° temperature difference between the insulation skin and its surroundings. Radiation is assumed negligible by comparison to 225 watts, (767 Btu/hr).

Outer film coefficient due to convection assumed to be: 3 Btu/hr-ft<sup>2</sup>°F.

$$Q_c = h_s A_s \Delta T_{\text{actual}}$$

$$\Delta T_{\text{act.}} = \frac{Q_c}{h_s A_s} = \frac{767}{3(7.5)} = 34^\circ$$

Actual skin temperature is 134°F instead of 125°F.

## APPENDIX

### Item 4 - HEAT-EXCHANGER OPTIMIZATION

The pertinent data necessary for the preliminary investigation of an optimum heat exchanger were obtained from experiments conducted on a laboratory reactor. This data included: (1) the mass flow rate, (2) the composition of the inlet gas, (3) the composition of the outlet gas, and (4) the system pressure. The thermal properties,  $k$ ,  $C_p$ ,  $\mu$ , were then computed for both the outlet and inlet gases based on the properties of the individual components at a mean temperature of 515°F. These computations indicated that there was no appreciable difference between the calculated values of the specific heat,  $C_p$ , thermal conductivity,  $k$ , and viscosity,  $\mu$ , of the inlet compared to the outlet gases.

The basic equations used for computing these quantities were<sup>1</sup>:

$$a. \quad C_{p_{mixture}} = \frac{\sum_{i=1}^n \frac{C_{p_i} (x_i M_i)}{n}}{\sum_{i=1}^n x_i M_i}$$

$$b. \quad \mu_{mixture} = \frac{\sum_{i=1}^n \frac{\mu_i x_i}{n}}{\sum_{j=1}^n x_j \phi_{ij}}$$

$$k_{mixture} = \frac{\sum_{i=1}^u \frac{k_i x_i}{n}}{\sum_{j=1}^n x_j \phi_{ij}}$$

where

$$\phi_{ij} = \frac{1}{\sqrt{8}} \left( 1 + \frac{M_i}{M_j} \right)^{-0.5} \left( 1 + \frac{\mu_i}{\mu_j} \right)^{0.5} \left( \frac{M_j}{M_i} \right)^{0.25}$$

- $n$  = number of chemical species present
- $x_i$  and  $x_j$  = mole fractions of species  $i$  and  $j$
- $M_i$  and  $M_j$  = molecular weight of species
- $C_{p_i}$  = heat capacity of species, Btu/lb°F
- $k_i$  = thermal conductivity, Btu-ft/ft<sup>2</sup>-hr°F
- $\mu_i$  = viscosity, lb/ft-hr

The results of the computations were

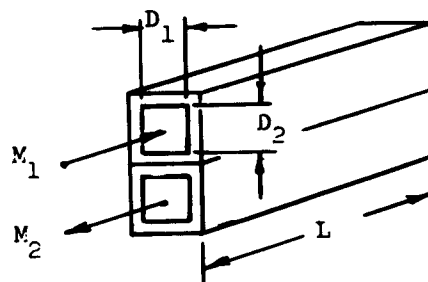
$$a. \quad C_{p_{mixture}} = 0.40 \text{ Btu/lb°F}$$

<sup>1</sup> Bird, R. B., Stewart, W. E., and Lightfoot, E. N., Transport Phenomena p. 25-28, Wiley & Sons, 1960.



- b.  $\mu_{\text{mixture}} = 5.95 \times 10^{-2} \text{ lb/ft-hr}$
- c.  $k_{\text{mixture}} = 0.050 \text{ Btu-ft/ft}^2\text{-hr}^\circ\text{F}$

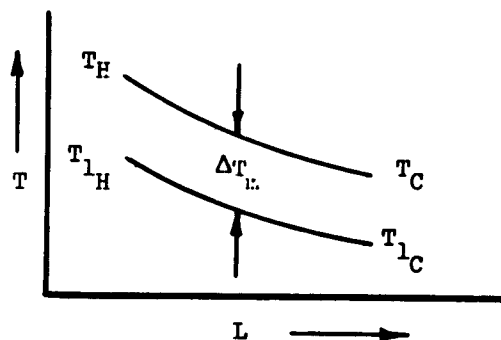
For analytical purposes, a simple tube arrangement, as shown in Figure 18 was selected as the basic heat exchanger. Two rectangular tubes of internal area  $2D_1D_2$  and length  $L$  are brazed together as shown. The mass flow rates  $M_1$  and  $M_2$  were considered to be equal. Tube sizes and material were limited to available stock items. The selection of the tubing was based on (1) an optimized internal cross-sectional area, (2) the smallest wall thickness for optimum heat transfer, (3) the largest value of thermal conductivity, (4) the smallest weight penalty per unit length, and (5) a material capable of withstanding temperatures in the vicinity of  $1400^\circ\text{F}$ . The most attractive commercially available tubing was considered to be square high copper alloy tubing.



SQUARE-TUBE HEAT EXCHANGER CROSS-SECTION

Figure 18

Figure 19 illustrates a temperature versus length diagram for a counter-flow heat exchanger with a constant mean temperature difference.



TEMPERATURE VS. LENGTH OF HEAT-EXCHANGER FOR COUNTER-CURRENT FLOW

Figure 19

Assuming that flow rates and heat capacities are the same in both inlet and outlet streams then the effectiveness of the heat exchanger under these conditions is:

$$(1) \quad E = MC_{p_m} (T_H - T_C) / MC_{p_m} (T_H - T_{1C})$$

$E$  = effectiveness, expressed as the ratio of the amount of heat transferred from the hot gas stream to the maximum amount that could be transferred from the hot gas stream

$M$  = mass flow rate, either outlet or inlet stream, lbs/hr

$C_{p_m}$  = heat capacity of gaseous mixture, either stream, Btu/lb°F

$T_H$  = temperature of outlet stream entering exchanger, °F

$T_C$  = temperature of outlet stream leaving exchanger, °F

$T_{1C}$  = temperature of inlet stream entering exchanger, °F

$T_{1H}$  = temperature of inlet stream leaving exchanger, °F

The actual rate of heat transferred,  $Q_T$ , from the outlet stream to the inlet stream is:

$$(2) \quad Q_T = MC_{p_m} (T_H - T_C) = MC_{p_m} E(T_H - T_{1C}), \text{ in Btu/hr.}$$

The mean temperature difference between the inlet and outlet gases is assumed to be constant and is given as:

$$(3) \quad \Delta T_m = (T_H - T_{1H}) = (T_C - T_{1C}) = (1 - E)(T_H - T_{1C})$$

The heat transferred is also expressed as the sum of the amount transferred by conduction and convection normal to the transfer surface plus the amount transferred by the extended surfaces (fins) created by the walls of the tubes. In terms of these amounts an expression for the length of each of the total number of tubes may be developed as follows:

$$(4) \quad L = \frac{Q_T/n}{\frac{h_l}{2} D_e \Delta T_m + T_m \sqrt{h_l k_c y_o} \tanh \left( D_e \sqrt{\frac{h_l}{k_c y_o}} \right)}$$

$L$  = length of each of  $n$  inlet tubes = length of each of  $n$  outlet tubes, ft

$k_c$  = thermal conductivity of tube material,  $\frac{\text{Btu/hr}}{\text{ft}^2 \cdot \text{hr}^\circ\text{F}}$

$y_o$  = inlet tube wall thickness = outlet tube wall thickness, ft

$n$  = number of parallel inlet tubes = number of parallel outlet tubes

$D_e$  = effective tube diameter = 4 x hydraulic radius, ft.

$$(5) \quad h_t = 0.023 \frac{k_m}{D_e} \left( \frac{M}{n D_e \mu_m} \right)^{0.8} \left( \frac{C_{p_m} \mu_m}{k_m} \right)^{0.4}$$

$h_t$  = surface film coefficient of heat transfer for tubes, both gases, Btu/hr-ft<sup>2</sup>-°F

$k_m$  = thermal conductivity of gas mixture, (calculated and found nearly identical for both gas mixtures), Btu-ft/ft<sup>2</sup>-°F-hr.

$\mu_m$  = viscosity of gas mixture (calculated and found nearly identical for both gas mixtures), lb/sec-ft.

The pressure drop created in the total heat exchanger due to flow is:

$$(6) \quad \Delta P = \frac{0.158}{\left( \frac{M}{h D_e \mu_m} \right)^{0.25}} \left( \frac{M^2 L}{h^2 g D_e^5 \rho_m} \right)$$

$\Delta P$  = pressure drop through 2L ft of tubing, lb/ft<sup>2</sup>

$g$  =  $4.17 \times 10^6$  ft/hr<sup>2</sup>

$\rho_m$  = density of gaseous mixture, lb/ft<sup>3</sup>

The power required to circulate the gases through the above pressure drop is expressed in terms of the weight penalty for providing this power as follows:

$$(7) \quad W_{\text{pump}} = 0.1313 MC_{p_1} T_{1C} \left[ \left( \frac{P_1 + \Delta P}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right]$$

$W_{\text{pump}}$  = weight penalty for pumping power, at 0.15 lbs mass per 1.0 watts, in lbs

$P_1$  = system pressure, lb/ft<sup>2</sup>

$\gamma$  =  $C_{p_m} / C_{v_m}$  (where  $C_{v_m}$  = specific heat at constant volume, in Btu/lb-°F)

The actual weight of the heat exchanger proper is as follows:

$$(8) \quad W_{\text{tube}} = w' 2Ln$$

$W_{\text{tube}}$  = weight of heat exchanger, lbs

$w'$  = weight per foot of inlet tube = weight per foot of outlet tube, lb/ft

The heat lost due to the inefficiency of the heat exchanger is also expressed in terms of the weight penalty for power to supply this lost heat, as follows:

$$(9) \quad W_{\text{eff}} = 0.0437 MC_{p_m} (1 - \eta)(T_H - T_{1C})$$

$W_{\text{eff}}$  = weight penalty for power required to make up for heat exchanger inefficiency, lbs

Similarly, the heat lost through the heat exchanger insulation in terms of weight penalty for power to supply this heat is:

$$(10) \quad W_{\text{power}} = 0.0437 n h_o L (D_e + 2y_o)(T_o - T_e)$$

$W_{\text{power}}$  = weight penalty for power required to make up for heat lost through heat-exchanger insulation, lbs

$h_o$  = surface film coefficient of heat transfer for insulation, Btu/hr ft<sup>2</sup>°F

$T_o$  = outer surface temperature of insulation, °F

$T_e$  = bulk temperature of surrounding gases, °F.

The weight of the insulation required around the heat exchanger is:

$$(11) \quad W_{\text{insul}} = \frac{(D_e + 2y_o) \rho_{\text{insul}} k_{\text{insul}} n L (2 - \eta) T_H + \eta T_{1C} - 2T_o}{2 \epsilon \sigma (T_o + 460)^4 - (T_e + 460)^4 + h_o (T_o - T_e)}$$

$W_{\text{insul}}$  = weight of insulation, lbs

$\rho_{\text{insul}}$  = density of insulation, lbs/ft<sup>3</sup>

$k_{\text{insul}}$  = thermal conductivity of insulation, Btu-ft/ft<sup>2</sup>°F-hr

$\epsilon$  = emissivity of insulation (dimensionless)

$\sigma$  = Stefan-Boltzman Constant =  $0.1712 \times 10^{-8}$  Btu/hr-ft<sup>2</sup>(°R)<sup>4</sup>

The actual numerical values of the variable used in the above equations (1) through (11) are as follows:

- (1)  $M$  = 9 lbs/hr
- (2)  $C_p$  = 0.4 B/hr-°F
- (3)  $T_n$  = 1400°F
- (4)  $T_{1C}$  = 75°F
- (5)  $T_e$  = 75°F
- (6)  $P_1$  = 3456 lbs/ft<sup>2</sup> abs.
- (7)  $\mu_m$  =  $5.95 \times 10^{-2}$  lbs/ft-hr
- (8)  $\rho_m$  =  $40.5 \times 10^{-3}$  lbs/ft<sup>3</sup>
- (9)  $k_c$  = 200 B/hr ft°F
- (10)  $k_m$  = 0.05 B/hr ft°F
- (11)  $h_o$  = 3 B/hr ft<sup>2</sup>°F
- (12)  $\rho_{\text{ins}}$  = 20 lbs/ft<sup>3</sup>
- (13)  $k_{\text{ins}}$  = 0.02 B/hr ft°F
- (14)  $\epsilon_{\text{ins}}$  = 0.9
- (15)  $g$  =  $4.17312 \times 10^8$  ft/hr<sup>2</sup>
- (16)  $\sigma$  =  $0.1712 \times 10^{-8}$  B/hr ft<sup>2</sup>°R<sup>4</sup>
- (17)  $\gamma$  = 1.4

The above mathematical development was programmed into the IBM 1620 computer at the MRD Division. An analytical study based on a weight penalty trade-off was then conducted to determine the optimum heat exchanger efficiency, tube diameter, length and configuration, tube weight, and insulation weight. In conducting the study a weight penalty of one pound for each 6.7 watts of power was used. This was based on a penalty of 0.05 lbs/watt for the power source and fuel, plus 0.10 lbs/watt for heat removal radiators.

The results of the trade-off study indicated that the optimum heat-exchanger efficiency should be 92% and that tube height and width should be approximately 0.32 inches. Two parallel inlet tubes counter-current to two parallel outlet tubes provide the optimum configuration. The actual weight of the exchanger proper was found to be 8 lbs, and of the insulation 2.5 lbs. The weight penalty for power to make up for heat-exchanger inefficiency, heat losses through insulation, and friction in pumping amounted to 22.4 lbs. The combined actual weight plus power penalty weight was 32.6 pounds.

<p>Aerospace Medical Division 6570th Aerospace Medical Research Laboratories, Wright-Patterson AFB, Ohio Rpt. No. AMRL-TDR-63-7. CARBON DIOXIDE REDUCTION SYSTEM. Final Report, Jan 63, vi + 83 pp incl illus., tables, 4 refs. Unclassified report</p> <p>An automatically operated carbon dioxide re- duction system was designed, fabricated and tested. The system will reduce 0.365 pounds of carbon dioxide per hour, equivalent to a 3.2 man carbon dioxide output, and is required for providing respiratory support for man on ex- tended space missions. The program was con- ducted in three phases, analysis of a reactor developed on a previous</p> <p>( over )</p>	<p>UNCLASSIFIED</p> <ol style="list-style-type: none"> <li>Carbon Dioxide Reduction System</li> <li>Closed Cycle Ecological System</li> <li>Ecology</li> <li>Space Flight</li> <li>AFSC Project 6373 Task 637302</li> <li>Life Support Systems Laboratory</li> <li>Contract AF 33(616)-8223</li> <li>MRD Division, General American Transportation Corp.</li> </ol> <p>UNCLASSIFIED</p>	<p>Aerospace Medical Division 6570th Aerospace Medical Research Laboratories, Wright-Patterson AFB, Ohio Rpt. No. AMRL-TDR-63-7. CARBON DIOXIDE REDUCTION SYSTEM. Final Report, Jan 63, vi + 83 pp incl illus., tables, 4 refs. Unclassified report</p> <p>An automatically operated carbon dioxide re- duction system was designed, fabricated and tested. The system will reduce 0.365 pounds of carbon dioxide per hour, equivalent to a 3.2 man carbon dioxide output, and is required for providing respiratory support for man on ex- tended space missions. The program was con- ducted in three phases, analysis of a reactor developed on a previous</p> <p>( over )</p>	<p>UNCLASSIFIED</p> <ol style="list-style-type: none"> <li>Carbon Dioxide Reduction System</li> <li>Closed Cycle Ecological System</li> <li>Ecology</li> <li>Space Flight</li> <li>AFSC Project 6373 Task 637302</li> <li>Life Support Systems Laboratory</li> <li>Contract AF 33(616)-8223</li> <li>MRD Division, General American Transportation Corp.</li> </ol> <p>UNCLASSIFIED</p>
<p>contract, experimental determina- tion of design parameters, and fabrication and testing of an improved engi- neering model. Operating characteristics, feed gas compositions, recycle flow rates, reaction temperatures and pressures, and catalyst composition and configuration were established and the effects of variations in these were determined. Recommendations are made for improving the system and for future work.</p>	<p>UNCLASSIFIED</p> <ol style="list-style-type: none"> <li>G. A. Remus, R. B. Neveril, J. D. Zeff</li> <li>In ASTIA collection</li> <li>Aval fr OTS:\$2.25</li> <li>Secondary report no. GATC Report No. MR-1163-50</li> </ol> <p>UNCLASSIFIED</p>	<p>contract, experimental determina- tion of design parameters, and fabrication and testing of an improved engi- neering model. Operating characteristics, feed gas compositions, recycle flow rates, reaction temperatures and pressures, and catalyst composition and configuration were established and the effects of variations in these were determined. Recommendations are made for improving the system and for future work.</p>	<p>UNCLASSIFIED</p> <ol style="list-style-type: none"> <li>G. A. Remus, R. B. Neveril, J. D. Zeff</li> <li>In ASTIA collection</li> <li>Aval fr OTS:\$2.25</li> <li>Secondary report no. GATC Report No. MR-1163-50</li> </ol> <p>UNCLASSIFIED</p>